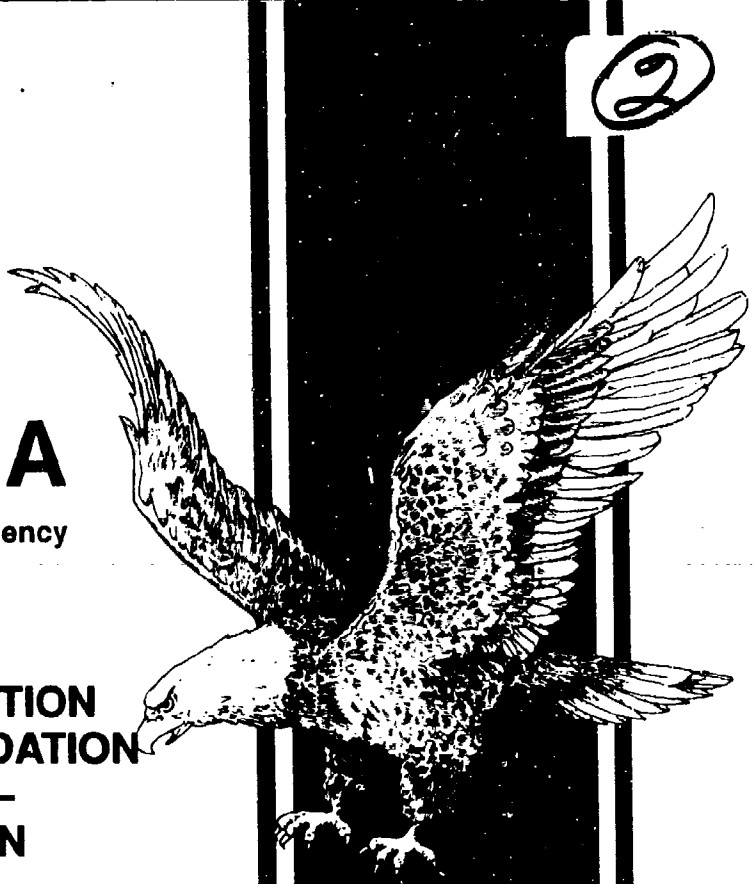
Final Report

USATHAMA

U.S. Army Toxic and Hazardous Materials Agency



BALL POWDER PRODUCTION WASTEWATER BIODEGRADATION SUPPORT STUDIES— WITH NITROGLYCERIN

(TASK ORDER NO. 11)

February 1989
Contract No. DAAK11-85-D-0008

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2

Final Report to
United States Army Toxic and Hazardous Materials Agency
February 1989

Ball Powder Production Wastewater Pilot-Scale Biodegradation Support Studies — With Nitroglycerin

(Task Order Number 11/Subtask 11.1)

Final Report

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) sponsored a pilot program at Badger Army Ammunition Plant (AAP) to evaluate two aerobic biological oxidation wastewater treatment technologies, extended aeration and sequencing batch reactor (SBR). Near the conclusion of the initial Arthur D. Little pilot study, Badger AAP personnel expressed a concern that the nitroglycerin (NG) concentration (8 mg/L) reported in the Point Source Survey[1] might be as much as 20 times too low. After discussions with USATHAMA personnel about the possibility of having approximately 200 mg/L NG in the wastewater stream, it was decided to extend the pilot test program to include two additional NG runs. The basis for this decision was threefold:

- the uncertainty surrounding the actual NG concentration in the wastewater stream;
- the lack of test results[2,3] showing the long-term (greater than one week) effect of NG at concentrations greater than 50 mg/L on biological treatment systems; and
- the necessity of having a complete test program in order to facilitate implementation of a full-scale system.

The objectives of the NG pilot test program were to determine: (a) the ability of both extended aeration and SBR systems to produce a treated wastewater capable of meeting anticipated National Pollutant Discharge Elimination System (NPDES) requirements when the ball powder wastewater contained NG; and (b) a better estimate of the actual concentration of NG likely to be in the wastewater.

Characterization of the ball powder wastewater stream showed an actual average NG inlet concentration of 192 mg/L. Pilot test results indicated that NG had a toxic effect on the biomass; and, therefore, neither system (extended aeration nor SBR) was able to consistently

meet anticipated NPDES limits. For a ten-day period at the beginning of the extended aeration test phase, NG was omitted form the wastewater. During this period, the analytes of concern (BOD, TSS, DPA, NDPA and DBP) were either below anticipated NPDES limits or trending downward.

Based on these results, we concluded that NG at a concentration of 150 to 200 mg/L caused a toxic effect on the biomass and recommended that two further areas be investigated, involving: (1) the identification and evaluation of technologies to pretreat ball powder wastewater to remove NG prior to aerobic biological oxidation treatment; and (2) bench- and/or pilot-scale testing to determine the limit of NG on biological treatment systems.

1.0 INTRODUCTION

Under Contract No. DAAK11-85-D-0008 with the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Process Development Branch, Arthur D. Little, Inc. was issued Task Order No. 3 entitled, "Propellant and Explosives Related Technology Development Studies," (Subtask 3.1: Treatment of Ball Powder Production Wastewater). Under this task order, we were requested to review and evaluate the currently available options for treating wastewater generated during the production of BALL POWDER® propellant* at Badger Army Ammunition Plant (AAP). Upon completion of this evaluation, the selection of the most promising technology for subsequent laboratory- and pilot-scale testing was to be made.

In actuality, two promising aerobic biological treatment technologies (activated sludge and rotating biological contactors) were selected for laboratory-scale testing. Upon completion of the laboratory testing and evaluation of the resultant data, one candidate technology was selected for pilot-scale testing. The actual pilot testing of the candidate technology (activated sludge treatment) was performed under Task Order No. 11 also entitled, "Propellant and Explosives Related Technology Development Studies," (Subtask 11.1: Ball Powder Production Wastewater Pilot-Scale Biodegradation Support Studies). Upon completion of the first phase of pilot testing, the recommendation was made to conduct an additional pilot test phase to determine the effect of nitroglycerin (NG) on this aerobic biological treatment process. This additional pilot testing was also performed under Task Order No. 11 (Subtask 11.1).

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* BALL POWDER propellant is a registered Trademark of Olin Corporation.

2.0 BACKGROUND

2.1 Badger AAP Wastewater

At the present time, ball powder is produced at only two locations in the United States, Badger AAP in Baraboo, Wisconsin and Olin Corporation's commercial facility in St. Marks, Florida. Badger AAP was constructed during World War II, operated intermittently from 1943 to 1975 and then placed in its present caretaker status. Due to the less stringent regulatory climate of that time and the fact that the plant ceased operations in 1975, no facility presently exists for treating wastewater generated if the plant were ever to resume operation. In contrast, St. Marks is a modern operating facility with an extended aeration wastewater treatment system capable of meeting National Pollutant Discharge Elimination System (NPDES) requirements. One might then suggest that a carbon copy of the St. Marks' wastewater treatment plant be installed at Badger AAP. However, it is not that simple since differences do exist between the two plants, and several of these differences have an effect on the composition of the wastewater generated. Consequently, there exists some uncertainty as to whether or not the treatment facility at St. Marks would be entirely compatible with the wastewater anticipated to be generated at Badger AAP.

Due to the plant's caretaker status, there currently is no NPDES permit. As a result, the treatment and effluent criteria for future generated wastewater was the point of discussion in preliminary meetings among Badger AAP, USATHAMA, Wisconsin Department of Natural Resources (WDNR), and Arthur D. Little, personnel. The major consensus reached during these meetings was that the overall concept of a "building block" approach to the treatment of Badger AAP wastewater would be the most appropriate plan of action. In addition, we estimated effluent discharge limitations (Table 2.1) which would have to be met by Badger AAP in the event operations were to resume. These effluent limitations were standard with respect to BOD and TSS (45 mg/L

TABLE 2.1

ESTIMATED WASTEWATER EFFLUENT LIMITATIONS

Parameter	Limit
pH	6.0 - 9.0
Biological Oxygen Demand (BOD)	30 mg/L avg
	45 mg/L daily
Nitrate (NO_3-N)	90 mg/L avg[a]
Sulfate (SO_4)	no limit assumed
Total Phthalates	detection limits[b]
Total Nitrosoamines	detection limits[b]
Total Suspended Solids (TSS)	50 mg/L avg
Total Dissolved Solids (TDS)	no limit assumed
Dissolved Oxygen (DO)	6-8 mg/L avg

[a] May or may not apply due to the absence of drinking water considerations.

[b] Based on EPA Method 625 for Base/Neutrals and Acids, the detection limit for DBP is 2.5 ug/L and for NDPA it is 1.9 ug/L

Source: Arthur D. Little, Inc. based on discussions with Wisconsin Department of Natural Resources.

daily, 30 mg/L average and 50 mg/L); however, they included restrictions to detection limits of 1.9 ug/L and 2.5 ug/L for N-nitrosodiphenylamine (NDPA) and dibutylphthalate (DBP), respectively.

A literature review of physical/chemical and biological treatment technologies lead to the selection of biological oxidation as the candidate technology for further study. However, due to the fact that a paucity of information existed on biological treatment of ball powder wastewater, it was decided that the first phase of this task would be a laboratory study whereby the two general classes of biological treatment systems (fixed film and suspended growth) could be evaluated. The laboratory tests were performed during February and March of 1987, and the results showed that, while both the rotating biological contactors (fixed film) and activated sludge (suspended growth) units met the anticipated NPDES requirements of 45 mg/L for BOD and detection limits (2.5 ug/L) for DBP, the RBCs seemed incapable of meeting the requirement of detection limits (1.9 ug/L) for DPA. The activated sludge units did not remove DPA to detection limits either, but the trend in these units was towards complete DPA removal as the biomass became acclimated, whereas the RBCs' removal efficiency of the NDPA did not appear to change with acclimation.

2.2 Badger AAP Pilot Study

Based on the results of the laboratory study,[4] we recommended that two types of activated sludge systems with low food to mass (F:M) ratios, extended aeration and sequencing batch reactor (SBR), be tested on a pilot-scale at Badger AAP. Extended aeration was selected because it is the most prevalent form of activated sludge operated at a low F:M ratio. The SBR was chosen even though it is not as prevalent as extended aeration, because it offers greater operating flexibility so as to accommodate varying wastewater feed rates and better control of the anoxic period for the removal of nitrates.

The objectives of the pilot program were twofold:

1) to determine the ability of the candidate biological oxidation system to produce a treated wastewater stream capable of meeting NPDES requirements; and

2) to develop preliminary design criteria for use in the ultimate engineering, design, and costing of a full-scale system.

To meet the objectives, a test plan[5] was developed and testing was performed over a period of eight months (September 1987 through April 1988). During that period, each of the two systems was operated for approximately four months using actual wastewater generated in Badger AAP's pilot ball powder production facilities. The wastewater was produced in a manner consistent with production in the full-scale ball powder lines with the exception that nitroglycerin (NG) was not added in the coating phase. The reason for omitting NG was to allow the wastewater samples to be shipped by air to the USATHAMA certified laboratory in Salt Lake City, Utah. It was felt that the omission of NG from the wastewater would not change the toxicity or biodegradability of the wastewater because it was predicted to be in low concentration (approximately 8 mg/L) by Olin's Point Source Survey[1].

Pilot test results[6] indicated that both of the systems were capable of meeting anticipated NPDES requirements (BOD, TSS, and NO_3-N), including detection limits for NDPA and DBP. The major difference between the two systems was the optimum F:M ratios, 0.11 day^{-1} for extended aeration and 0.14 day^{-1} for SBR. This difference in F:M ratios resulted in the SBR being slightly more efficient removing organics

In addition to meeting NPDES requirements, neither the extended aeration nor the SBR systems was difficult to operate or had any maintenance problems that would appear to be of concern in a full-scale

system. However, the SBR system was easier to operate and maintain, due to the fact that it was computer controlled and operated without a separate clarifier.

Based on the results of the pilot test program, a preliminary design was developed for both systems (Table 2.2). The most notable differences between these two systems are:

- Extended aeration requires a 30% larger reactor volume than the SBR;
- Extended aeration requires two 3,750 ft^2 clarifiers while the SBR requires none; and
- Extended aeration requires nearly 25% less oxygen than the SBR.

2.3 NG Pilot Study

Near the conclusion of the initial pilot study, Badger AAP personnel expressed a concern that the NG concentration (8 mg/L) from the Point Source Survey[1] might be as much as 20 times too low. After discussions with USATHAMA personnel about the possibility of having approximately 200 mg/L NG in the wastewater stream, it was decided to extend the pilot test program to include two additional NG runs. The basis for this decision was threefold:

- the uncertainty surrounding the actual NG concentration in the wastewater stream;
- the lack of test results showing the long term (greater than one week) effect of NG at concentrations greater than 50 mg/L on biological treatment systems; and
- the necessity of having a complete test program in order to facilitate implementation of a full-scale system.

TABLE 2.2

PRELIMINARY DESIGN SUMMARY

Biological Reactor	Extended Aeration	SBR
Reactor Volume	7.3 million gal	5.7 million gal
Number of Reactors	2	3
Hydraulic Retention Time	60 hr	45 hr
Biomass Growth	7,130 lb/day	7,130 lb/day
Biomass Retention Time	30 days	23 days
Nitrogen Supplied	0 lb/day	0 lb/day
Phosphorus Supplied	250 lb/day	250 lb/day
Aeration System		
Biological Oxygen Requirement	980 lb/hr	1,200 lb/hr
Air Flow Rates (STP)	4,000 ft^3/min	4,880 ft^3/min
Clarifier		
Percent Recycle	77%	NA
Clarifier Area	7,500 ft^2	NA
Number of Clarifiers	2	NA
Dimensions of each Clarifier		
o Diameter	70 ft	NA
o Depth	15 ft	NA
Sludge Dewatering and Disposal		
Sludge dewatered	86,000 gal/day	86,000 gal/day
Sludge to disposal	35,700 lb/day	35,700 lb/day

NA - Not Applicable

3.0 OBJECTIVES OF NG TEST PROGRAM

Due to the uncertainty surrounding the concentration of NG in ball powder wastewater and the degradation of NG by aerobic bacteria, a pilot program was undertaken with the following objectives: 1) to determine the concentration of NG in the ball powder wastewater stream; 2) to determine the ability of each biological system to meet NPDES limitations in the presence of NG; and 3) to determine if modifications to the preliminary design, based on the earlier pilot study results[6] were needed due to the presence of NG.

4.0 WASTEWATER CHARACTERIZATION

The full-scale manufacture of ball powder propellant produces wastewater containing a complex mixture of organic and inorganic constituents including substantial amounts of nitrocellulose (NC) and NG which are major components in the production of double based propellants. The wastewater also contains the solvent ethyl acetate (which comprises a significant portion of the BOD), collagen, a dibutylphthalate (DBP) plasticizer, and a diphenylamine (DPA) stabilizer. The major inorganic component is sodium sulfate that is used to help dehydrate the ball powder prior to coating.

The composition of the wastewater produced for Badger AAP's pilot-scale biological treatment facility is very similar to that of a full-scale ball powder line. The pilot plant used the same raw materials for the manufacture of ball powder which are used in full-scale production, including NG. Since NG does appear in the wastewater, it was necessary to transport the water samples by ground transport to a local laboratory for analysis.

Wastewater for the Badger AAP pilot-scale treatment facility was produced batchwise on a weekly basis by a pilot-scale ball powder propellant manufacturing line also located on the Badger AAP site. The small scale production line generated approximately 600 gallons of wastewater per week; 300 gallons from the hardening operation and 300 gallons from the coating process. During production, the Badger AAP operators transferred the wastewater to a 600-gallon stainless steel tank on a trailer and then transported the wastewater to the pilot-scale treatment facility upon completion of a batch. The wastewater was then pumped into two, 300-gallon holding tanks located adjacent to the biological reactor. The weekly production of 600 gallons of wastewater was sufficient to supply the biological treatment system for one week, even during periods of maximum feeding. At the end of each week, any unused wastewater remaining in the holding tanks was pumped to a sanitary sewer and the tanks were thoroughly cleaned in preparation for a fresh batch of wastewater.

The holding tanks also provided a point at which the wastewater could be adjusted to meet the nutrient requirements of the biomass. Based on the general rule of thumb -- for every 100 ppm BOD, 5 ppm nitrogen and 1 ppm phosphorous are required, it was not deemed necessary to add a nitrogen source to the wastewater. The bacteria were able to retrieve ample nitrogen from the ammonia molecules that were by-products of collagen degradation in the wastewater. The fresh wastewater contained an average 5 ppm ammonia nitrogen, but the total Kjeldahl nitrogen averaged a much higher 57 ppm.

The phosphorous level in the raw wastewater was, on average, 1 ppm which does not meet the requirement. Therefore, in order to ensure that an excess of phosphorous was available to the bacteria, a sufficient quantity of phosphoric acid was added to each batch of wastewater to produce an inlet stream with a phosphorous content of 5-10 mg/L.

Strongly alkaline or acidic wastewater may adversely affect the activity and health of microorganisms thereby making it necessary to adjust the wastewater feed to a neutral pH. However, the average pH value of the Badger AAP wastewater was 7.2; and therefore required no buffering before entering the biological reactor.

During the Badger AAP pilot-scale test program, it was found that storing the raw wastewater in holding tanks changed the inlet concentrations to the biological reactor significantly over the seven day holding period. The degradation, which occurred in the holding tanks via anaerobic bacteria already present in the wastewater, is comparable to what would happen in an equalization basin for a full-scale biological treatment facility. Table 4.1 summarizes the average concentrations of various analyzed components in the wastewater at the beginning and end of the seven-day holding period (See Appendix A for weekly, initial and final, concentrations).

According to data in Table 4.1, there was significant degradation of carbonaceous material occurring in the holding tanks. The average initial BOD was 760 mg/L and the average final was 567 mg/L showing a 25% drop in BOD levels over the seven day holding period. Similarly, the COD levels dropped 21% over seven days.

The other concentrations of the organic compounds in the wastewater also changed dramatically from the first to the seventh day of the holding period. Ethyl acetate concentrations were reduced 45% from an average 247 mg/L to 136 mg/L. This large reduction is due to the volatilization of ethyl acetate as well as bacterial degradation during storage. The non-volatile organics also showed a dramatic reduction during the holding period due to anaerobic bacterial degradation. The nitroglycerin concentration dropped an average of 24% from 192 mg/L to 146 mg/L. DBP was reduced 65%, from 0.6 to 0.2 mg/L; DPA concentrations dropped 6%, from 2.2 to 2.1 mg/L; and NDPA concentrations dropped 60% from 0.2 to 0.1 mg/L.

The change in inorganic compounds, though less dramatic, is still quite evident. The nitrate nitrogen (NO_3-N) concentrations shown in Table 4.1 illustrate a 13% drop from the average initial concentration of 31 mg/L to a final average concentration of 27. The anoxic bacteria in the holding tanks utilized some of the oxygen contained in nitrates as an oxygen source, while reducing the nitrates. It was expected that the anoxic bacteria would also utilize sulfates in the wastewater as a source of oxygen and thereby reduce the sulfate concentration. Sulfate was not monitored often enough in the feed wastewater to draw a conclusion based on sulfate data alone. However, since the vast majority of total dissolved solids (TDS) is sodium sulfate, a reduction in TDS concentration would largely be due to a reduction in the sulfate concentration. Table 4.1 shows an average reduction in TDS concentrations of 84 mg/L over the five day storage period. There was also a faint hydrogen sulfide odor emitted from the holding tanks; evidence of the reduction of sulfate to hydrogen sulfide by anoxic

TABLE 4.1

CHANGE IN WASTEWATER COMPOSITION
DURING SEVEN DAY HOLDING PERIOD

Component Analyzed	Average Initial Concentration (mg/L)	Average Final Concentration (mg/L)	Average (%) Reduction
BOD	760	567	25
COD	1206	955	21
Ethyl Acetate	247	136	45
Nitroglycerin	192	146	24
DBP	0.6	0.2	65
DPA	2.2	2.1	6
NDPA	0.2	0.1	60
NO_3-N	31	27	13
Total Dissolved Solids	3782	3698	2
Ammonia	5	6	22*
Total Kjeldahl Nitrogen	59	57	3

* Ammonia nitrogen levels increased 22% during the seven day holding period.

Source: Arthur D. Little, Inc.

bacteria. Consequently, hydrogen sulfide emissions from a large equalization basin could be a potential odor problem during unfavorable atmospheric conditions if the wastewater was held for too long.

In the storage tanks, the anoxic bacteria partially degraded the collagen with the concurrent release of ammonia derived from the protein molecules. Although Table 4.1 shows a 22% increase in ammonia nitrogen concentrations during the seven day storage period, there were no noticeable ammonia fumes and the TKN values dropped only 3% during that time. The TKN concentration reflects the total nitrogen contained in the collagen and ammonia molecules indicating that, while ammonia was formed upon degradation of the collagen, it remained in solution and was not volatilized into the atmosphere.

5.0 PILOT-SCALE TESTING

5.1 Pilot Plant Operation

The NG pilot-scale test program at Badger AAP investigated the use of two activated sludge systems, extended aeration and SBR, for the treatment of ball powder production wastewater with NG. The two biological wastewater treatment pilot plants were operated alternately from the beginning of August 1988 through October 1988, beginning with the SBR. The SBR tests were conducted for approximately 30 days and operated at a F:M ratio of 0.14 day^{-1}. The extended aeration test program was operated at the conclusion of the SBR test phase and ran for approximately 25 days with a F:M ratio of 0.11 day^{-1}. In both cases, the F:M ratios were based on the optimal conditions determined in the initial pilot test phase.

During the week between the operation of the SBR and the extended aeration unit, the biological system was operated in the extended aeration configuration with wastewater that did not contain NG. The week-long operation without NG was not scheduled at the onset of the NG test program, but was added when the toxicity of the ball powder wastewater with NG was observed during the SBR testing. By monitoring the biological system to determine if it would approach the level of operation that was observed during the initial pilot test phase (without NG), we expected to determine whether the NG was causing the toxic effects. After the week-long operation without NG, the extended aeration system was fed actual wastewater containing NG, and the planned test program was completed.

As can be seen from Figures 5.1 and 5.2, the extended aeration and SBR systems had the same equipment set-up as the initial test phase. Both biological pilot systems were designed with a 300-gallon inlet storage tank (T1) in which the wastewater was stored upon delivery from the ball powder production pilot unit. Any additional wastewater that was delivered from the pilot unit was stored in an auxiliary 300-gallon

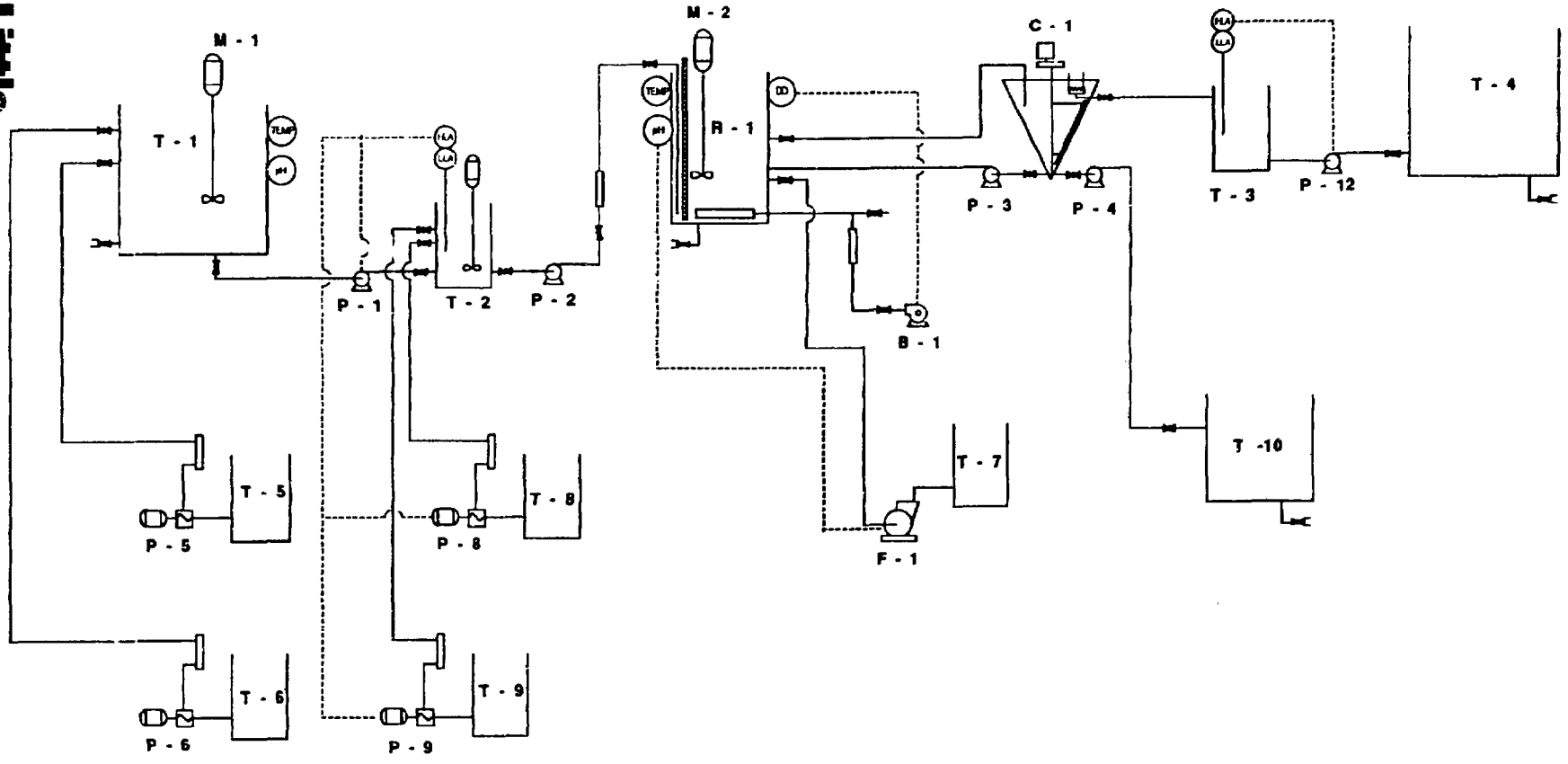
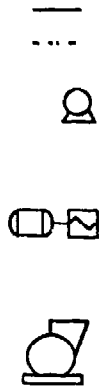


Figure 5.1
Process Schematic For Extended Aeration Pilot Plant

Source: Arthur D. Little, Inc

Notes For Extended Aeration Process Schematic



Piping

Control Lines

Self-Priming Centrifugal Pump
- P - 1 Transfer Pump

Peristaltic Pumps
- P - 2 Feed Pump
- P - 4 Biomass Waste Pump
- P - 10 Effluent Pump

Diaphragm Pump
- P - 5 Sodium Hydroxide pump
- P - 6 Sulfuric Acid Pump
- P - 8 Ammonium Hydroxide Pump
- P - 9 Phosphoric Acid Pump

Screw Feeder
- F - 1 Calcium Carbonate Feeder

B - 1 Air Compressor

Mixer
- M - 1 Equalization Tank Mixer
- M - 2 Reactor Mixer

pH Meter

Temperature Indicator

Dissolved Oxygen Meter

High Level Alarm

Low Level Alarm

Scraper

Ball Valve

Effluent Weir

Rotameter

Clarifier

Influent Tanks
- T - 1 Wastewater
- T - 2 Surge Tank

Effluent Tanks
- T - 3 Effluent Overflow
- T - 4 Effluent Storage
- T - 10 Biological Sludge Storage

Chemical Feed Tanks
- T - 5 Sodium Hydroxide
- T - 6 Sulfuric Acid
- T - 7 Calcium Carbonate
- T - 8 Ammonium Hydroxide
- T - 9 Phosphoric Acid

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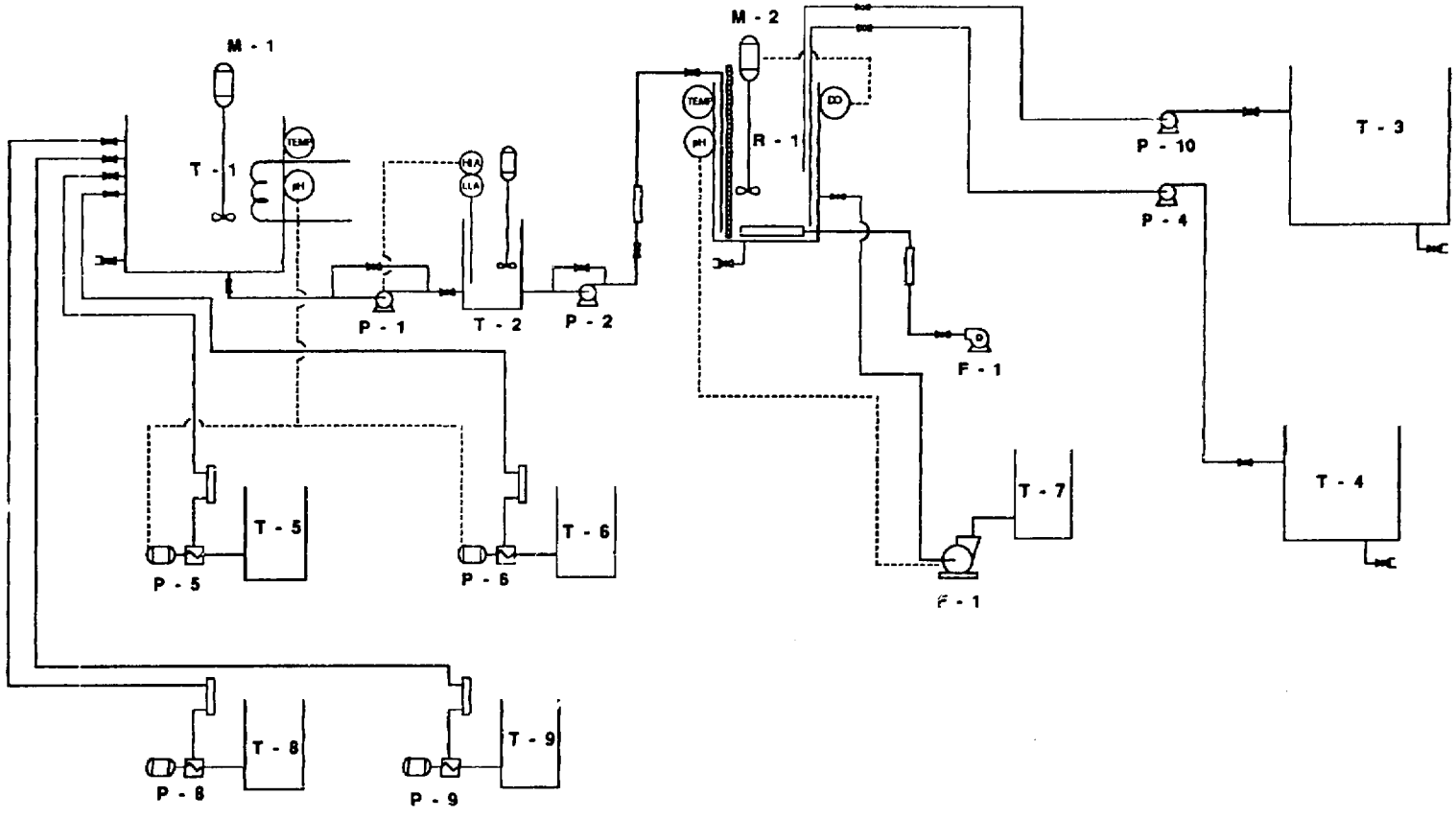

Figure 5.2
Process Schematic For Sequencing Batch Reactor Pilot Plant

Source: Arthur D. Little, Inc

Notes For Sequencing Batch Reactor Process Schematic

Piping

Control Lines

Self-Priming Centrifugal Pump
- P - 1 Transfer Pump

Peristaltic Pumps
- P - 2 Feed Pump
- P - 4 Biomass Waste Pump
- P - 10 Effluent Pump

Diaphragm Pump
- P - 5 Sodium Hydroxide pump
- P - 6 Sulfuric Acid Pump
- P - 8 Ammonium Hydroxide Pump
- P - 9 Phosphoric Acid Pump

Screw Feeder
- F - 1 Calcium Carbonate Feeder

B - 1 Air Compressor

Mixer
- M - 1 Equalization Tank Mixer
- M - 2 Reactor Mixer

pH Meter

Temperature Indicator

Dissolved Oxygen Meter

High Level Alarm

Low Level Alarm

Ball Valve

Effluent Weir

Rotameter

Influent Tanks
- T - 1 Wastewater
- T - 2 Surge Tank

Effluent Tanks
- T - 3 Effluent Overflow
- T - 4 Effluent Storage
- T - 10 Biological Sludge Storage

Chemical Feed Tanks
- T - 5 Sodium Hydroxide
- T - 6 Sulfuric Acid
- T - 7 Calcium Carbonate
- T - 8 Ammonium Hydroxide
- T - 9 Phosphoric Acid

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tank. In addition to using T1 for main storage, it was also used as the point for nutrient addition (nitrogen, phosphorous, and pH control) as and when required. T1 was provided with an air mixer that insured a homogeneous wastewater supply to the 100-gallon surge/settling tank (T2). T2 was utilized as the feed tank to the biological reactor as well as a settling tank for any suspended solids that could be readily settled. From T2 the wastewater was pumped to the biological reactor using a small peristaltic pump.

Both biological reactors were operated at volumes of about 80 to 90 gallons during the entire NG test program and were the contact point between the raw wastewater and the biomass. The method of operation of the reactor defined whether the process was an extended aeration or SBR treatment system. In the extended aeration system, the reactor was operated on a continuous basis with a constant F:M ratio as well as a constant dissolved oxygen concentration. In contrast, during the operation of the SBR, the biological reactor was operated batchwise with a variable F:M ratio and an anoxic period within each cycle. Figure 5.3 shows the typical operation of the SBR cycle for Run 3.1.

The SBR used the reactor for the entire biological oxidation process; from the actual oxidation of the carbonaceous material to the settling and decantation of the biomass and effluent, respectively. In comparison, the extended aeration system used the reactor only as a point for carbonaceous oxidation. The biomass was settled in a separate clarification system (C-1) where the effluent exited via an overflow weir near the top of the clarifier and the settled biomass was either recirculated to the reactor or wasted as necessary. The treated effluent from the top of the clarifier was collected in a 300-gallon storage tank (T10) for analysis prior to its release (per Badger AAP instruction) to Badger's industrial sewer.

During the settle phase of the SBR cycle, the biomass was allowed to settle in a quiescent reactor. At the conclusion of the settle phase, 20 gallons of effluent were decanted from the biological reactor and

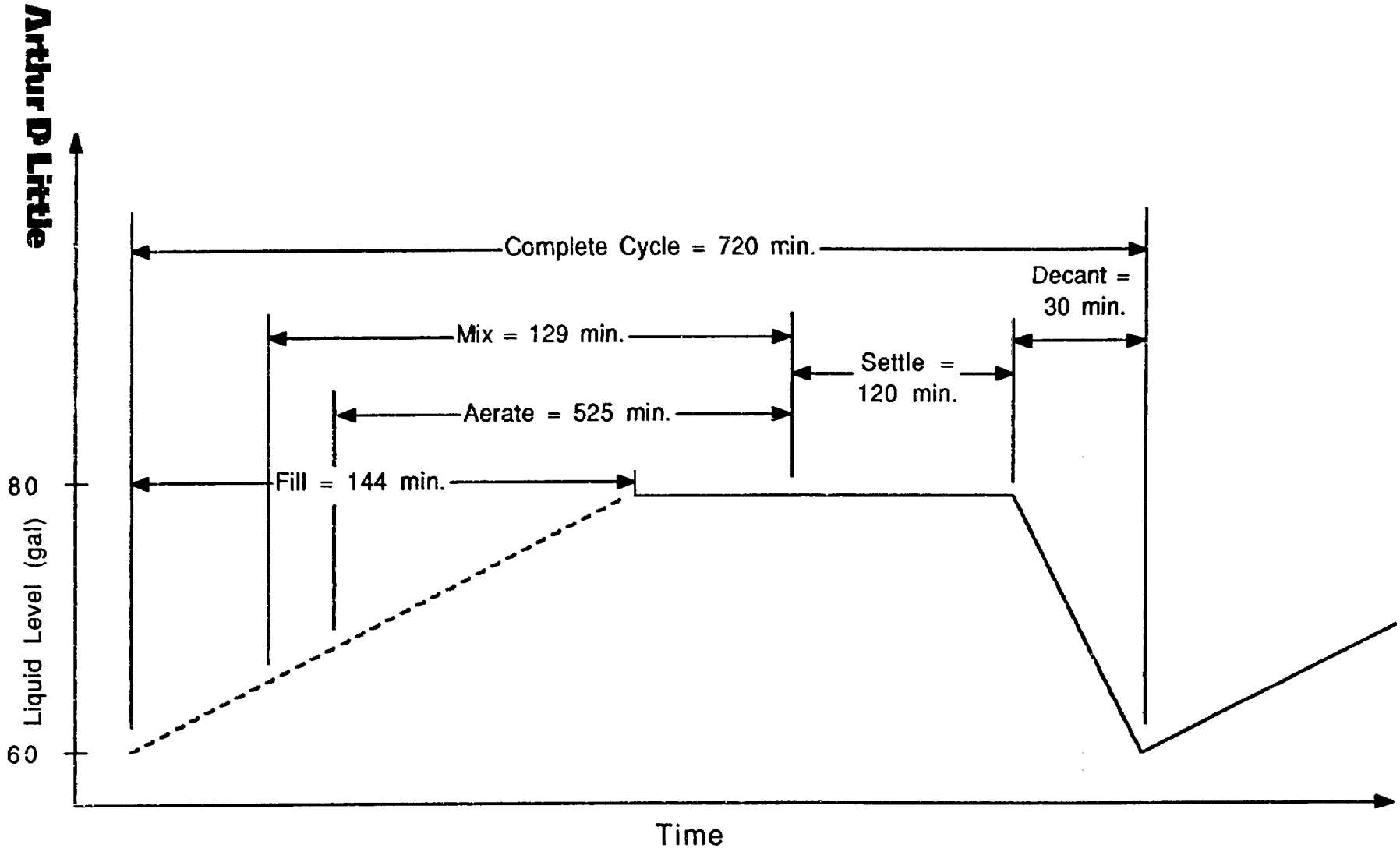


Figure 5.3
SBR Cycle Times

Source: Arthur D. Little, Inc.

stored in T10 until the effluent could be analyzed prior to its release to Badger's industrial sewer. In the SBR system, all the biomass remained within the biological reactor, thereby eliminating the need for a sludge recycle stream. However, as necessary, biomass was wasted from the bottom of the biological reactor in order to maintain a constant mixed liquor suspended solids (MLSS) concentration in accordance with the NG pilot program test plan.

5.2 Start-Up of the Biological Reactors

At the conclusion of the initial pilot program in April of 1988, the ball powder pilot plant was put in a standby mode and the biological treatment plant was fed synthetic wastewater until the NG test program began on July 25, 1988. During the intervening three and one-half months, the biological reactor was operated in the SBR mode with a F:M ratio of approximately 0.14 day^{-1}. The reason for using the same biomass in the NG test program was to avoid the two-week acclimation period that was needed with biomass from Baraboo's Municipal Wastewater Treatment Facility. This was a viable option because the ball powder wastewater had shown no toxic effect on the biomass and no buildup of toxins in the biomass during the previous two runs.

Therefore, on July 25, 1988, the SBR pilot test was begun using actual ball powder wastewater with NG and acclimated biomass. The first week of the test was used to allow the biomass to equilibrate prior to evaluating the SBR's ability to treat wastewater containing NG. During that week, close observation was kept on the dissolved oxygen (DO) uptake rate, MLSS, and visual appearance of the biomass, both on a macroscopic and microscopic level. The DO uptake rate was consistently low (0.1 mg/L/min) and never rose to the 0.3 mg/L/min rate that was observed during the initial pilot program.

In addition to the respiration problems, the NG appeared to have a toxic effect on the biomass. The biomass died at a steady rate and formed a layer of dead biomass on top of the reactor. This layer of

dead biomass was also observed in the acclimation period of the initial test program, but in that case, it occurred immediately after the reactor had been seeded and decreased steadily over the first week. By the time the actual test runs without NG were begun, the layer of dead biomass completely disappeared. However, in the NG pilot program, the layer of dead biomass never ceased and caused a steady decrease in the MLSS concentration over the test program (see Section 5.5). Another symptom of the toxic effect of NG was the decrease in the number of protozoa in the biomass during the equalization period. At the start of the equilization period there were numerous protozoa, and after five days there were almost none. The low DO uptake rate, the death of the biomass and the absence of protozoa lead to the conclusion that NG did have a toxic effect on the system.

5.3 Test Parameters

Table 5.1 presents the major test parameters for both runs of the NG pilot program and the ranges to which they were held. F:M ratio was the major parameter that differed during the two runs. In each of the runs, the F:M ratio was set based on the optimum operating conditions determined in the initial pilot program. Figure 5.4 graphically depicts the F:M ratio. From this graph one can determine exactly how the F:M ratio was varied for the two test runs. The fluctuation of F:M ratio during a given test run was due to the constant degradation of the carbonaceous material in a given batch of inlet wastewater over a week's time (see Section 4.0).

Another major variable in the operation of any biological system is the concentration of DO in the wastewater. DO concentration in the biological reactor affects many different components of the treatment systems. For example, at high DO concentrations, the settling of the biomass can be greatly affected, and at low DO concentrations, the substrates that are removed, either carbonaceous or nitrogenous, are greatly affected. Initially, the DO concentration in the biological reactor was maintained using a DO controller. However, given the small

TABLE 5.1

BIOLOGICAL OXIDATION PILOT-SCALE TESTING WITH NG

Run No.	Experiment Description	F:M	BOD Inlet Conc. (mg/L)	Microbe Conc. (mg/L)	O_c (Day)	Dissolved Oxygen Conc. (mg/L)	Flow Rate (gal/day)	HRT (hr)	Sludge Recycle Rate (gal/day)	Sludge Wasting Rate[c] (gal/day)
3.0	SBR	0.14[a]	760	3,500 5,200[b]	35	1 - 3	52	37	NA	0
4.0	Extended Aeration	0.11	760	3,500	35	1 - 3	40	48	40	0

NA - Not Applicable

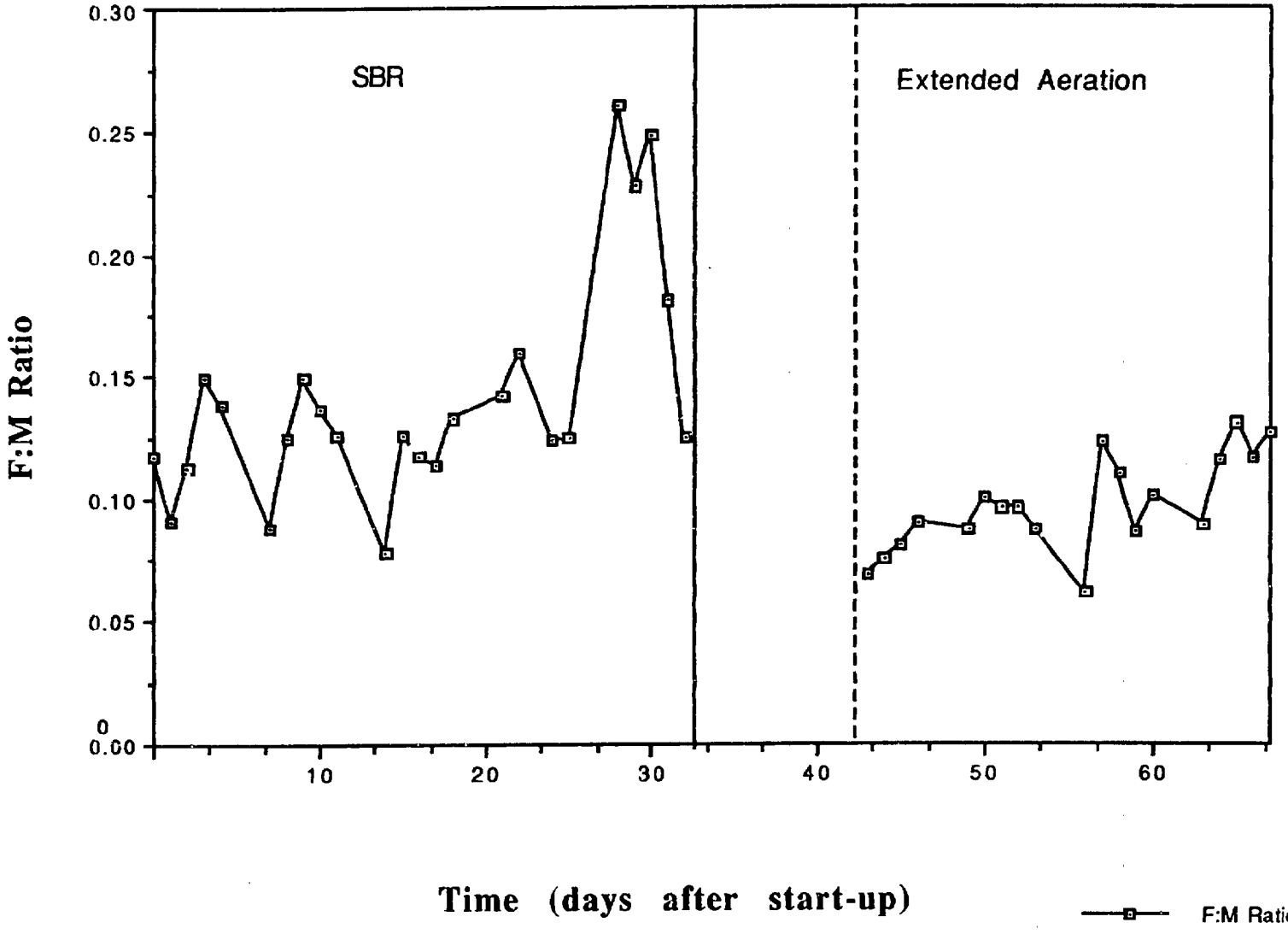
[a] F:M ratio is calculated after fill phase.

[b] After decant phase, wastewater volume is 2/3 of the original volume.

[c] Sludge wasting was not necessary due to the toxic effect of NG on the biomass.

Source: Arthur D. Little, Inc.

FIGURE 5.4
F:M Ratio vs. Time



Source: Arthur D. Little, Inc.

size of the reactor and the fact that a coarse bubble diffuser was used to supply the oxygen to the biological reactor, the controller could not be fine tuned to hold the DO concentration in the desired 1 to 3 mg/L range. Therefore, the DO concentration was controlled by a timer. The timer was programmed to turn the blower on for a sufficient length of time to increase the DO concentration in the wastewater to approximately 3 mg/L and then to turn the blower off for a period of time to allow the system to utilize the excess oxygen in the reactor until the level dropped to approximately 1 mg/L.

The determination of the time periods during the extended aeration tests was straightforward. Since the F:M ratio remained fairly constant throughout any given extended aeration run, the oxygen utilization rate was also constant. Therefore, the length of time required to utilize 2 mg/L of oxygen was estimated using the biomass concentration and the DO utilization rate of the bacteria.

Control of the DO concentration in the SBR system was much more complicated; however, the reason was the variation in the F:M ratio that occurs from phase to phase during an individual cycle in the SBR system. Because the F:M ratio decreases over the entire cycle, the required DO concentration is higher in the beginning of the cycle then it is at the end. This decrease in the DO uptake rate from the beginning of the cycle to the end made it difficult to use a single timing sequence as the only means of controlling the DO concentration in the biological reactor. In order to alleviate this problem, we designed two separate time cycles; one for the react-fill phase; the other for the react phase. While this did not allow us to consistently keep the DO concentration between 1 to 3 mg/L, it did permit much better control then would have been achieved using only one time cycle.

Another major difference between the SBR and extended aeration systems is the existence of anoxic phases in the SBR system. The first two anoxic SBR phases occur at the beginning of the cycle during static fill and mix fill phases. No oxygen is supplied to the biomass during

these two phases with the intent to remove any nitrates or nutrients that must be controlled. The other phases in which no oxygen is supplied to the SBR are the settle, decant, and idle phases. Unlike the first two phases, mix fill and static fill, these phases cannot be removed from the SBR cycle if they are undesired. Therefore, anoxic stages are a by-product of the SBR system.

Full-scale extended aeration systems, such as biological oxidation ditches, have anoxic zones as well, that are created by the distance the wastewater has traveled from the aerator. However, to replicate an anoxic zone of this type on a pilot-scale was neither cost effective nor practical. In addition, companies have been designing and building biological oxidation ditches to utilize 30 mg/L NO_3-N and companies such as Eimco Process Equipment Co. have significant amounts of data on full-scale systems to support these conclusions.

5.4 Wastewater Treatment

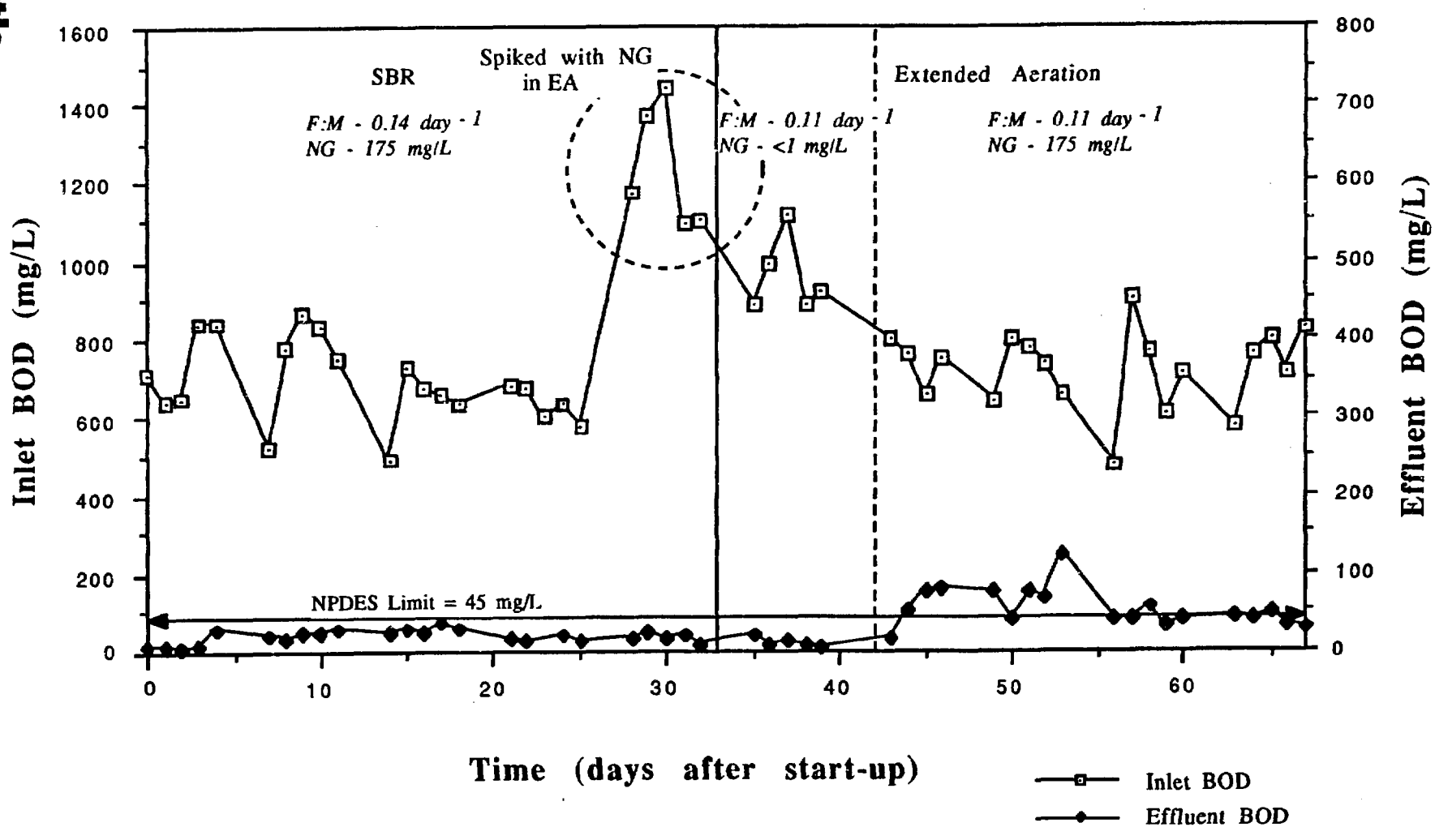
The following section covers the ability of both the SBR and extended aeration to meet anticipated NPDES limits when NG is in the feed. The tabular data for each constituent is presented in Appendix B for the SBR run and Appendix C for the extended aeration run.

5.4.1 Carbonaceous Material Removal

For the NG pilot tests the results for the daily BOD and COD analyses of the inlet and effluent streams are shown in Figures 5.5 and 5.6, respectively. The graph of BOD vs Time (Figure 5.5) indicates that the SBR was capable of meeting the daily NPDES BOD limit (45 mg/L) but not the average NPDES BOD limit (30 mg/L). The graph also shows that the extended aeration unit could not meet either NPDES limit for BOD consistently when NG was in the feed stream.

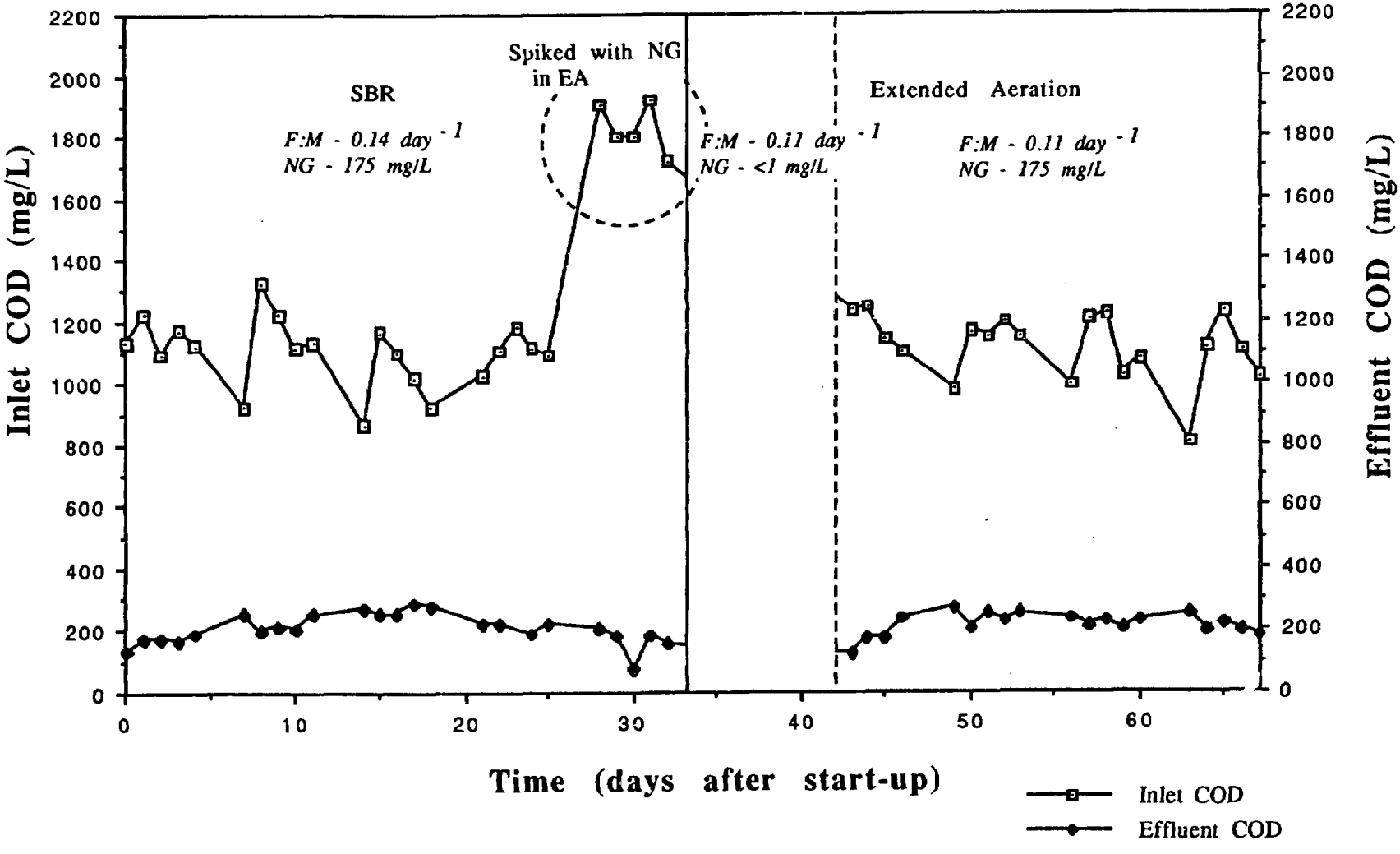
For approximately 10 days at the beginning of the extended aeration test run, the biological system was fed wastewater that did not

FIGURE 5.5
BOD vs. Time



Source: Arthur D. Little, Inc.

FIGURE 5.6
COD vs. Time



Source: Arthur D. Little, Inc.

contain NG. This period is also shown on the graph of BOD vs Time (Figure 5.5) between days 33 to 43. During this period, the effluent BOD was at its lowest value and was consistently below the anticipated NPDES BOD limit (45 mg/L daily and 30 mg/L avg.). On day 43, wastewater with NG was again fed to the extended aeration unit, and the effluent BOD began to rise.

Neither the SBR nor the extended aeration unit removed BOD as efficiently with the NG in the wastewater and neither met anticipated NPDES BOD limits. However, when the NG was removed from the wastewater, the extended aeration system quickly recovered and met anticipated NPDES BOD limits. The improved performance of the extended aeration system when no NG was fed led to the conclusion that NG adversely affected the biomass' ability to remove BOD from the wastewater stream.

5.4.2 Degradation of EPA Priority Pollutants

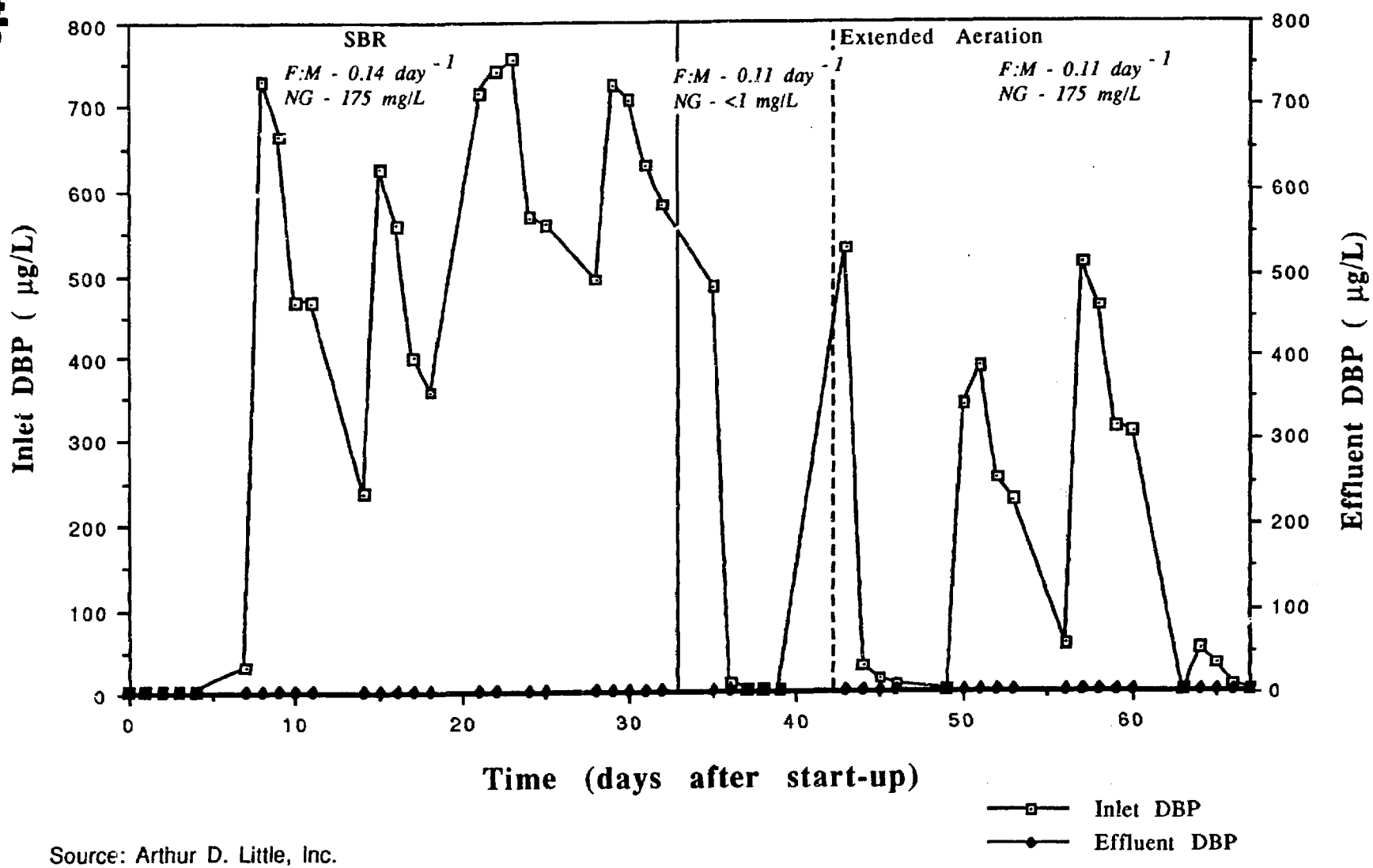
5.4.2.1 DBP

Figure 5.7 shows the DBP results for the inlet and effluent streams during the SBR and extended aeration test phases. One can see from the graph that the DBP concentration in the effluent was never above the anticipated NPDES limit (detection limit, 2.5 μg/L) during the 67 days of operation. Consequently, the presence of NG in the wastewater appeared to have no effect on DBP removal.

5.4.2.2 DPA and NDPA

The analytical method used for the analysis of NDPA in the initial test phase was the EPA's Method 625-Base/Neutrals and Acids (Appendix D). This method is EPA-approved for NDPA; however, the NDPA is subject to thermal decomposition to DPA in the gas chromatograph (GC) inlet. Because of the decomposition of NDPA it is not possible to separate the DPA from the NDPA, and the results were a sum total of both DPA and

FIGURE 5.7
DBP vs. Time



Source: Arthur D. Little, Inc.

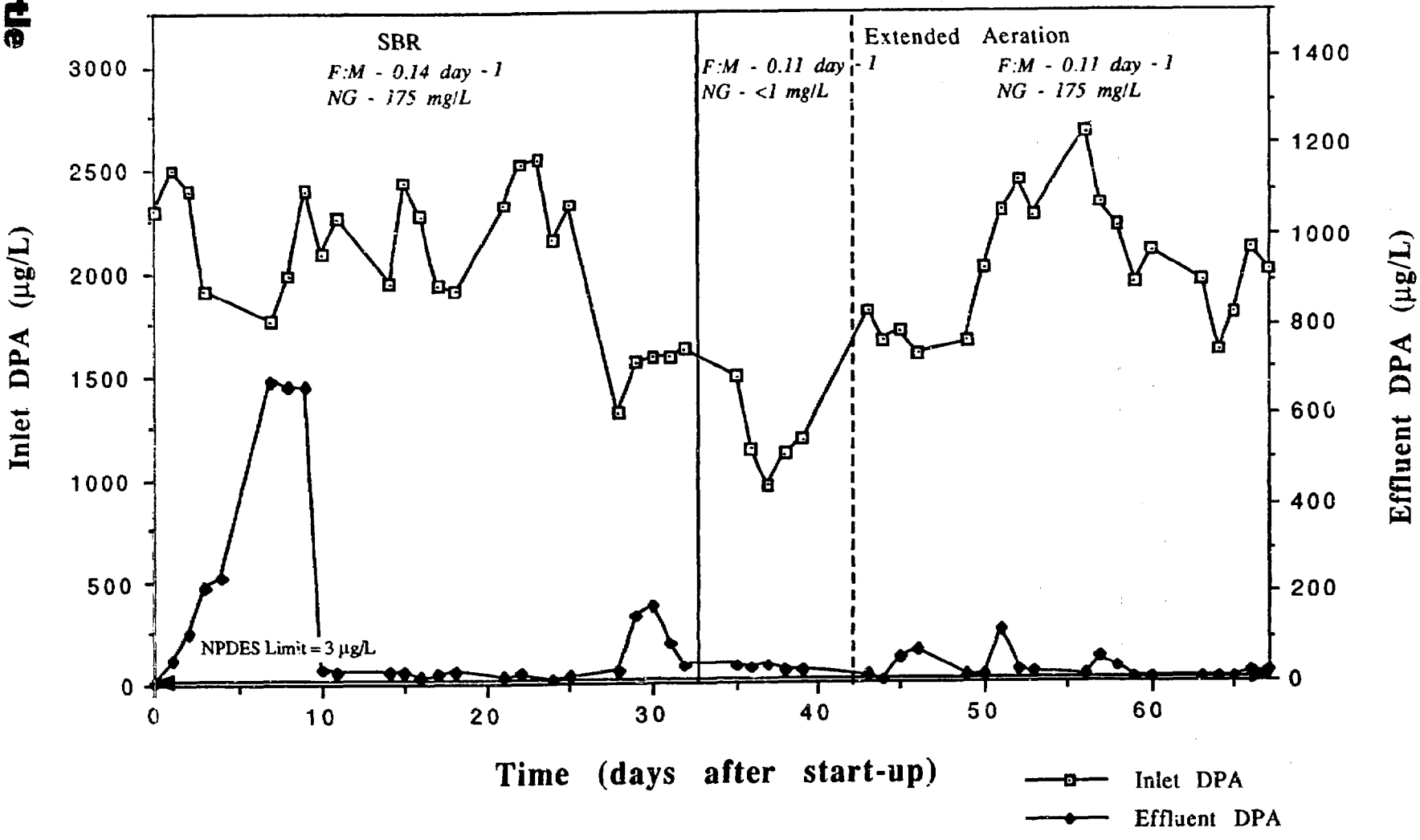
NDPA. This number was felt to be a worst case scenario and that if the biological reactor could remove the sum of the DPA and NDPA to Method 625 detection limit (1.9 μg/L), the optimum operating condition would be conservative.

Method 625 was expected to be used for the analysis of NDPA in the NG pilot tests as well; however, during the equilibration week for the SBR unit, a problem was detected with the analytical method. The problem originated because the NG degraded in the GC inlet and subsequently caused the degradation of both the DPA and the NDPA. The degradation of the NDPA and DPA resulted in the analytical procedure showing less than detection limit in every sample including the inlets and matrix spikes. Because of the difficulties with Method 625, a new HPLC method was developed to analyze for NG, DPA, NDPA and DBP. The method is summarized in Appendix D. With the ambient HPLC injection port, the NDPA did not decompose to DPA as it did in Method 625 allowing both NDPA and DPA to be separated during the analysis.

Figures 5.8 and 5.9 are graphs of DPA and NDPA vs Time, respectively, and show that neither biological system was capable of meeting the anticipated NPDES limit for NDPA (detection limit, 1.9 μg/L). The week during the extended aeration test program where no NG was added to the wastewater showed a downward trend in the effluent concentration of DPA (Figure 5.8), but even then the values never reached the EPA Method 625 detection limit. The NDPA effluent concentration during the same time period showed similar decreases, but the trend was not consistently downward and also did not meet the anticipated NPDES limit for NDPA (1.9 μg/L).

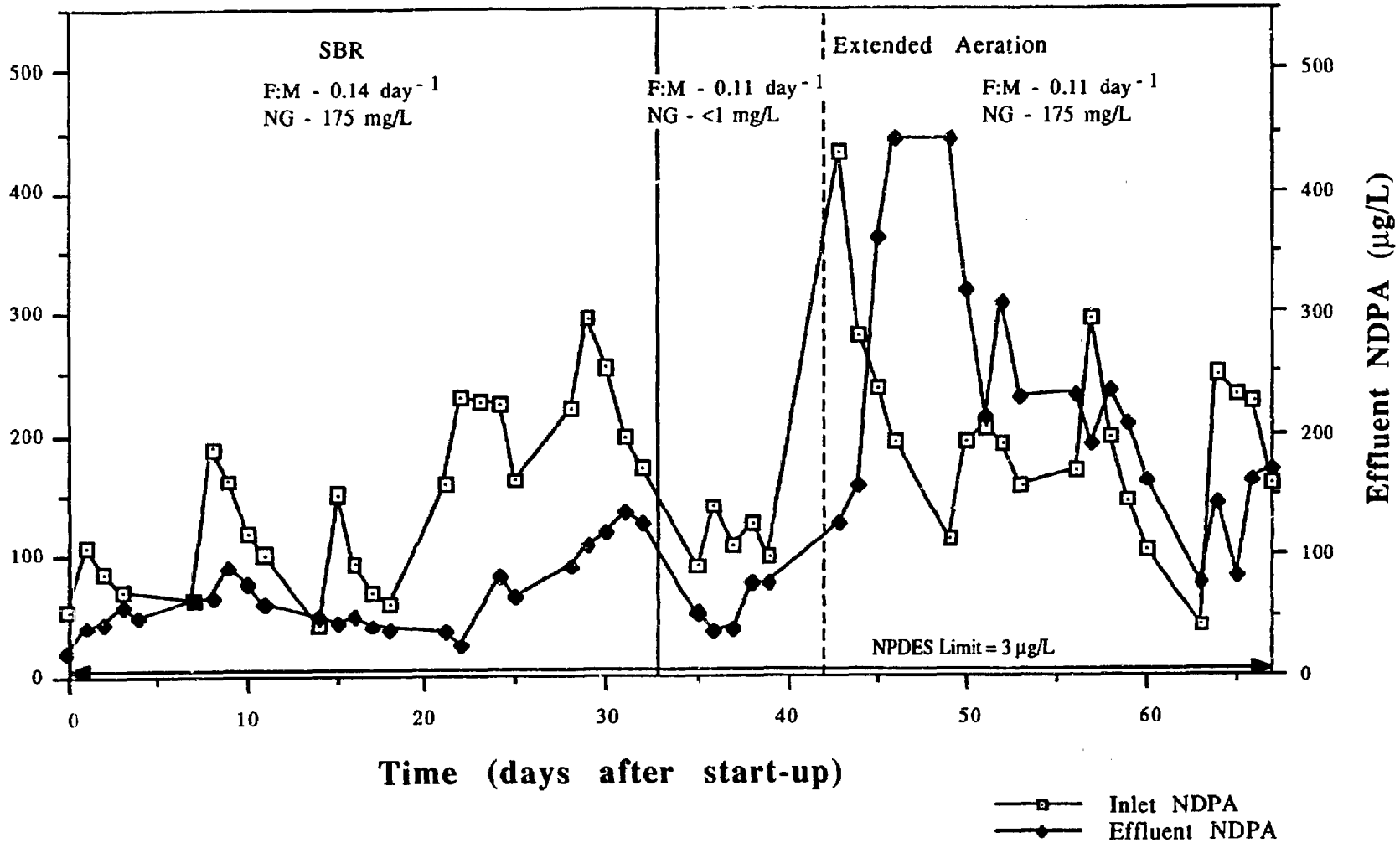
The significantly higher effluent concentrations of DPA and NDPA, as compared to concentrations in the initial test phase (without NG), led to the conclusion that NG adversely affected the biomass' ability to degrade both DPA and NDPA. The biological system was also slower to respond to the deletion of the NG with respect to the NDPA and DPA than

FIGURE 5.8
DPA vs. Time



Source: Arthur D. Little, Inc.

FIGURE 5.9
NDPA vs. Time



Source: Arthur D. Little, Inc.

with respect to BOD. In order for the system to recover and degrade the DPA and NDPA as efficiently as seen in the initial test phase, it would require more than the one week time period allotted.

5.4.3 NG

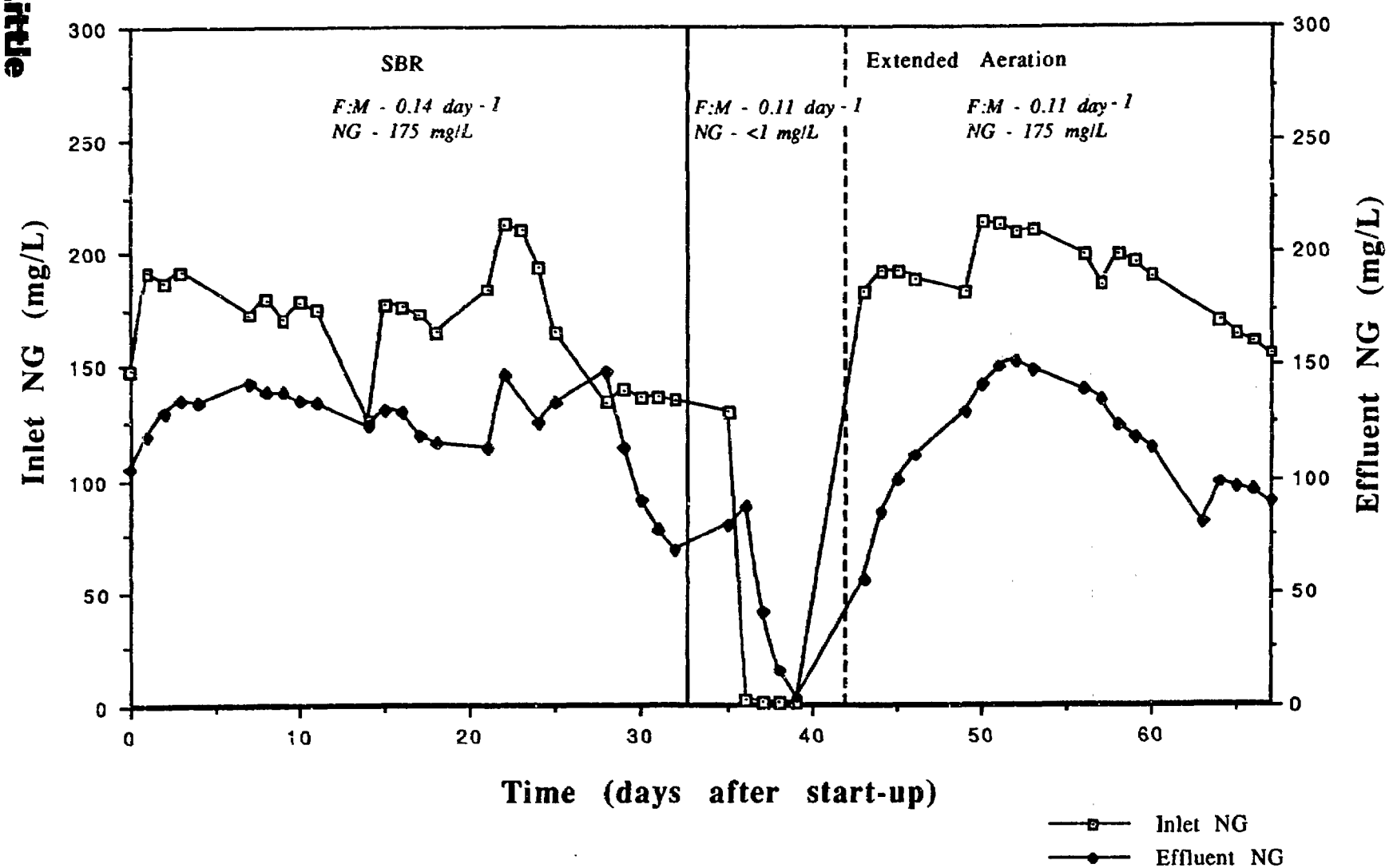
The inlet and effluent NG concentrations for both test runs are shown in Figure 5.10. The results of both the SBR and the extended aeration unit show that approximately 40% of the NG is biologically degraded. During the extended aeration test, the first 10 days were operated without NG (days 33 to 43). The wastewater for this period was prepared in the same manner as it was during the initial test phase where NG was not added to the ball powder production coating phase and extra ethyl acetate was added in its place.

5.4.4 Nitrates

The wastewater generated in Badger AAP's ball powder manufacturing operations contains very little NO_3-N other than that bound in the NG. Additional NO_3-N is produced in the biological reactor as a result of the aerobic metabolization of the nitrogen found in the collagen. Figure 5.11 shows the inlet NO_3-N concentration which averaged approximately 31 mg/L.

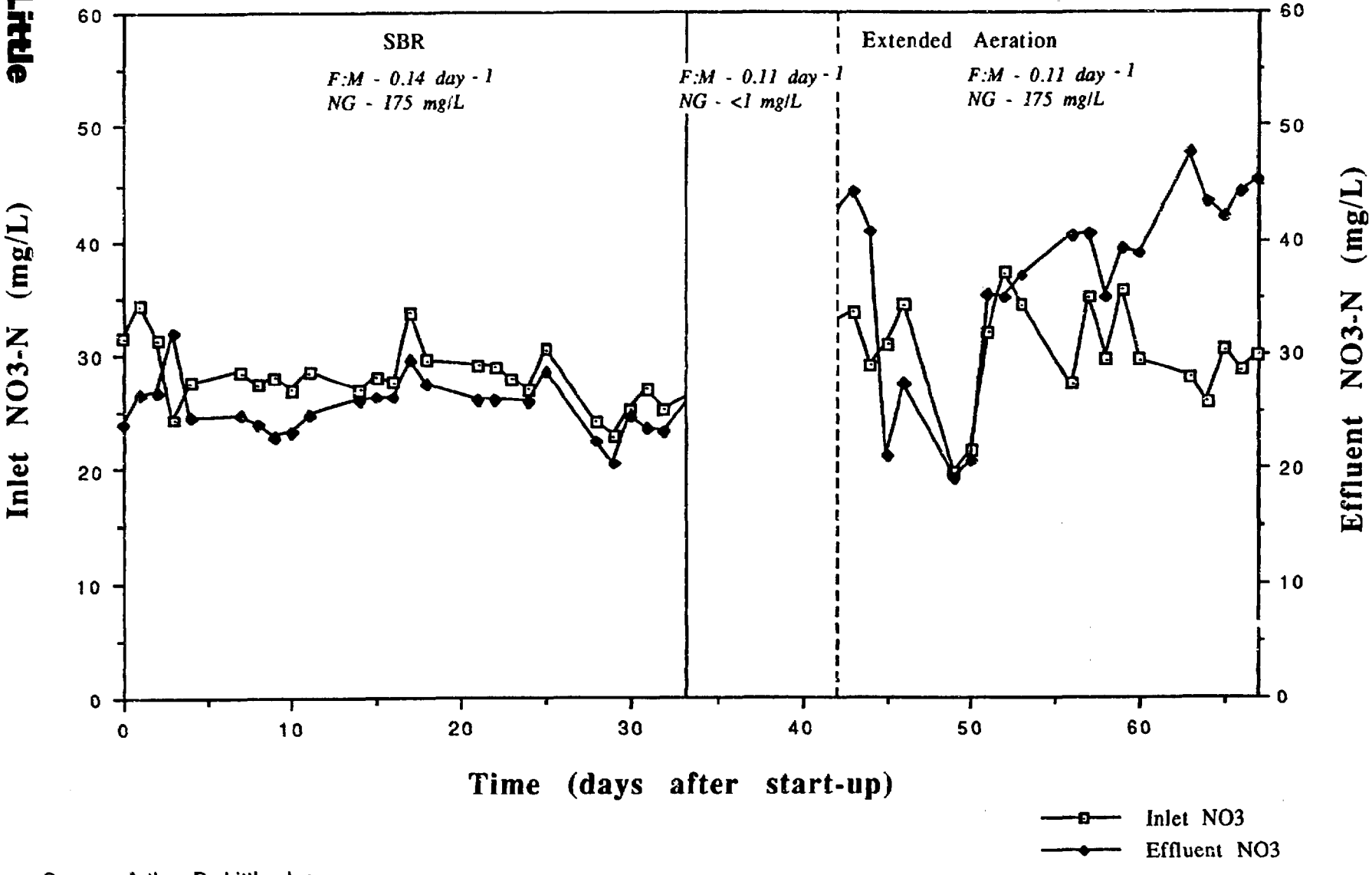
Both the SBR and the extended aeration systems experienced no difficulties meeting the anticipated NO_3-N NPDES limit (50 mg/L). The extended aeration system, however, had higher concentrations of NO_3-N in the effluent than did the SBR. The higher concentration of NO_3-N was caused by the lack of an anoxic zone in the extended aeration system where denitrification could occur. However, the extended aeration system used in the pilot program does not give an accurate representation of a full-scale system's ability to treat NO_3-N because a full-scale system, such as a biological oxidation ditch, would have anoxic zones simply by virtue of its size and the location of its aerators.

FIGURE 5.10
NG vs. Time



Source: Arthur D. Little, Inc.

FIGURE 5.11
NO3 vs. Time



Source: Arthur D. Little, Inc.

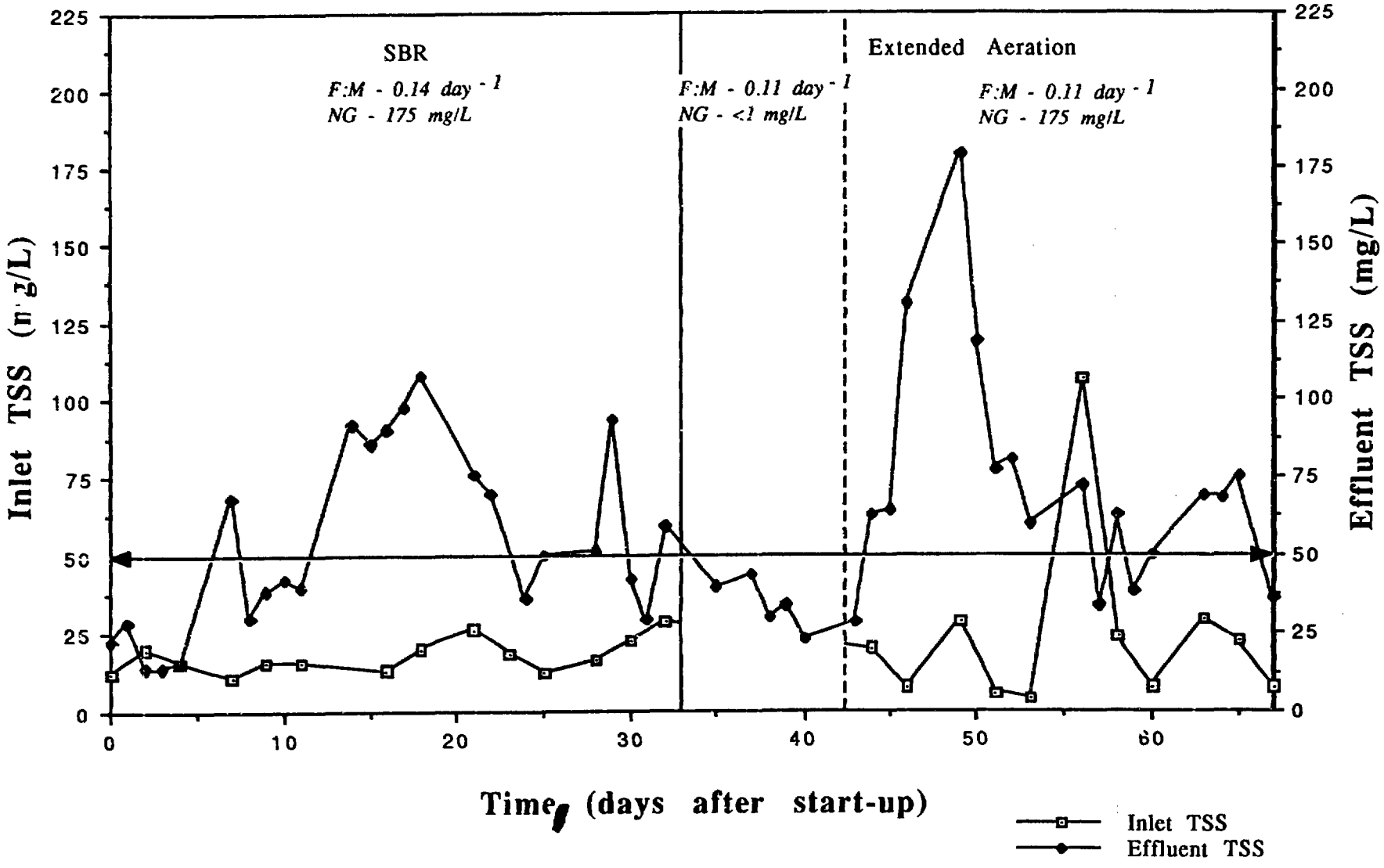
During talks with EIMCO Process Equipment Company, the subject of NO_3-N removal by their biological oxidation ditches was discussed, and they presented data from full-scale facilities that were capable of removing 20-30 mg/L NO_3-N through denitrification in anoxic zones. Therefore, if it becomes necessary for Badger AAP to meet a drinking water standard for NO_3-N (20 mg/L) instead of the current anticipated NPDES limit (50 mg/L), a full-scale biological oxidation ditch should have no difficulty in removing the additional 20-30 mg/L of NO_3-N as easily as an SBR. This assumption is based on the degradation of the NG because the NG pilot test results indicate that neither system can utilize NO_3-N that is bound in the NG molecule.

5.4.5 Total Suspended Solids

During the SBR and extended aeration test runs (Figure 5.12), the TSS concentrations were consistently above the anticipated NPDES limit (50 mg/L). The high concentrations of TSS in the effluent, most of which appeared to be dead biomass, caused the excursions in BOD in the effluent stream (Figure 5.13). As shown in Figure 5.13, the soluble effluent BOD was significantly below the anticipated NPDES BOD limit (45 mg/L daily and 30 mg/L ave), and only the additional BOD from the TSS increased the effluent BOD to above the anticipated NPDES limit.

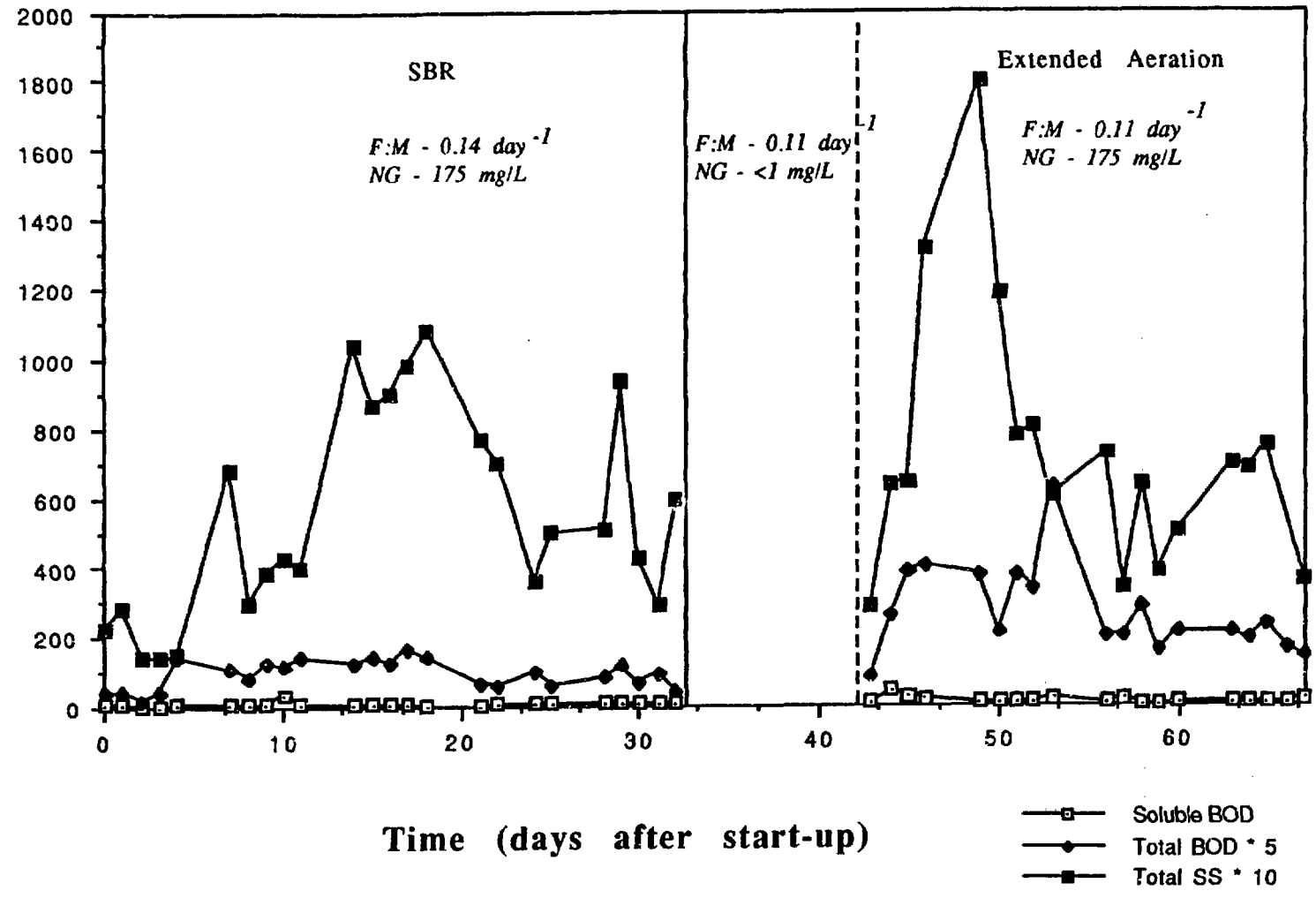
The first 10 days of the extended aeration phase were operated with wastewater that contained no NG. During this period, the TSS in the effluent were consistently below the anticipated NPDES limit (50 mg/L) and exhibited a downward trend. At the conclusion of the 10 days, wastewater containing NG was fed to the system, and the TSS effluent concentration began to rise to well above the anticipated NPDES limit. At the same time, a layer of dead biomass formed on the surface of the reactor. In addition to not meeting the NPDES limit for TSS, the loss of biomass in the effluent caused a steady decline in the MLSS concentration (see Section 5.5). Based on these results, it can be concluded that the NG was toxic to the biomass.

FIGURE 5.12
TSS vs. Time



Source: Arthur D. Little, Inc.

FIGURE 5.13
BOD and TSS vs. Time



Source: Arthur D. Little, Inc.

5.5 Effects on Biomass

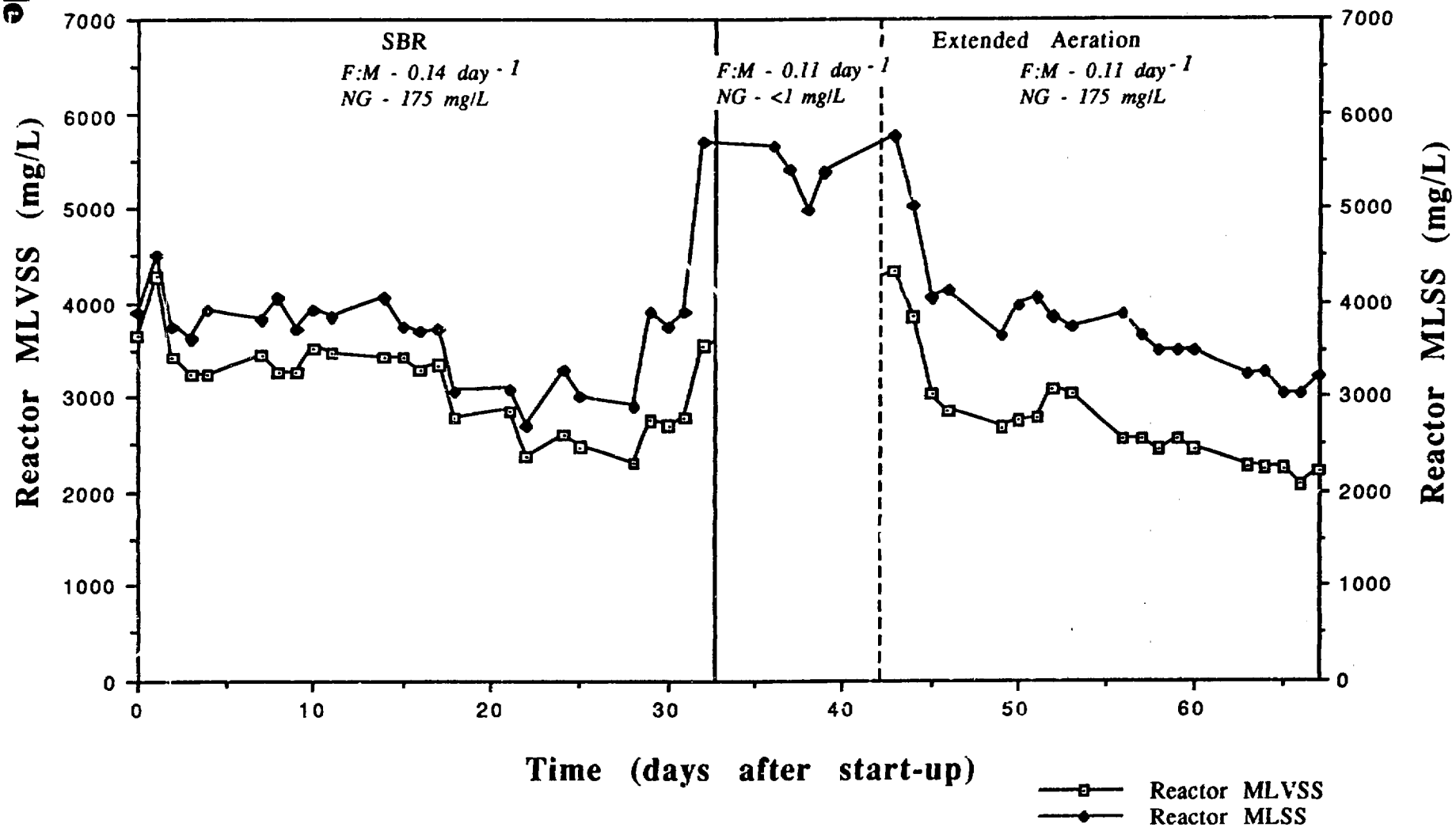
5.5.1 Quantity and Content of the Biomass

Monitoring the various types of microorganisms living in the biomass and the relative size of their population is useful in evaluating the effectiveness of a particular activated sludge system. The quantity of bacteria existing in the sludge can be estimated by analyzing the mixed liquor volatile suspended solids concentration (MLVSS) in the reactor. It is more difficult to determine the types of microorganisms in the biomass because the heterotrophic and autotrophic bacteria are impossible to see under a standard microscope. It is useful, however, to check for existing populations of rotifers, amoeba, and other protozoa which can be seen under a microscope, as they indicate the stability of a system.

In order to quantify the total concentration of bacteria in the biomass, samples from the reactor were analyzed for MLVSS. The MLVSS value represents the concentration of organic material in the biomass, most of which is bacteria. MLSS concentrations were also determined for reactor samples because the turnaround time for that test is much shorter and the MLSS numbers closely track the MLVSS concentrations (see Figure 5.14). The shorter turnaround time allows a daily monitoring of the size of the bacterial population which is important in maintaining a stable system. The relationship between these two parameters is shown in Figures 5.15 and 5.16.

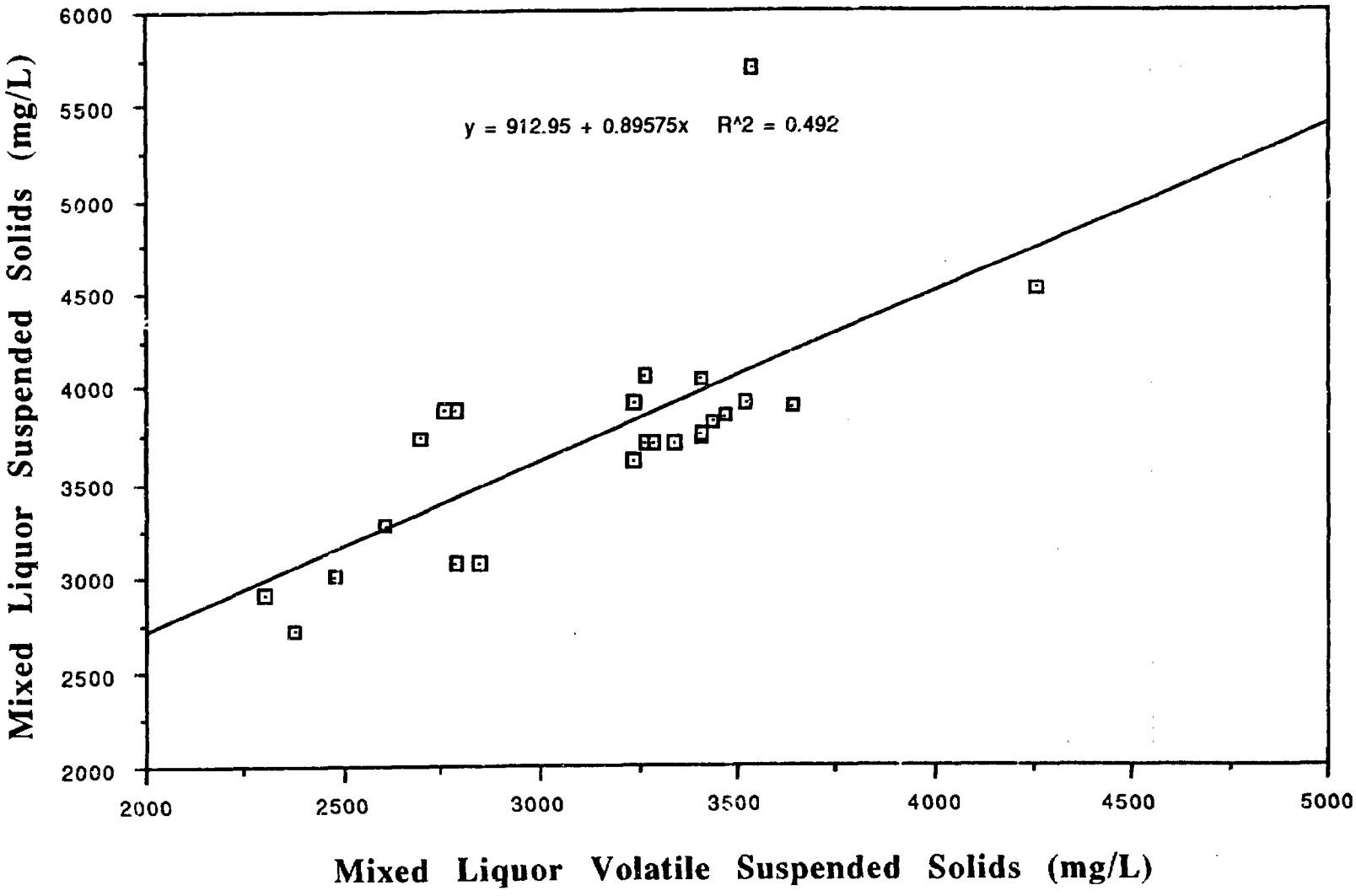
Prior to adding NG to the system, several types of protozoa were found living in the biomass. During times of poor settling in the reactor or clarifier, one can see a predominance of filamentous and amoeboid microorganisms indicative of an unstable system. But during optimum conditions when a clear supernate was achieved after settling, a larger number of rotifers and cilliates can be found signifying stability. However, after the addition of NG, there were no signs of any protozoa living in the biomass. In addition, the MLSS and MLVSS values began to

FIGURE 5.14
MLVSS and MLSS vs. Time



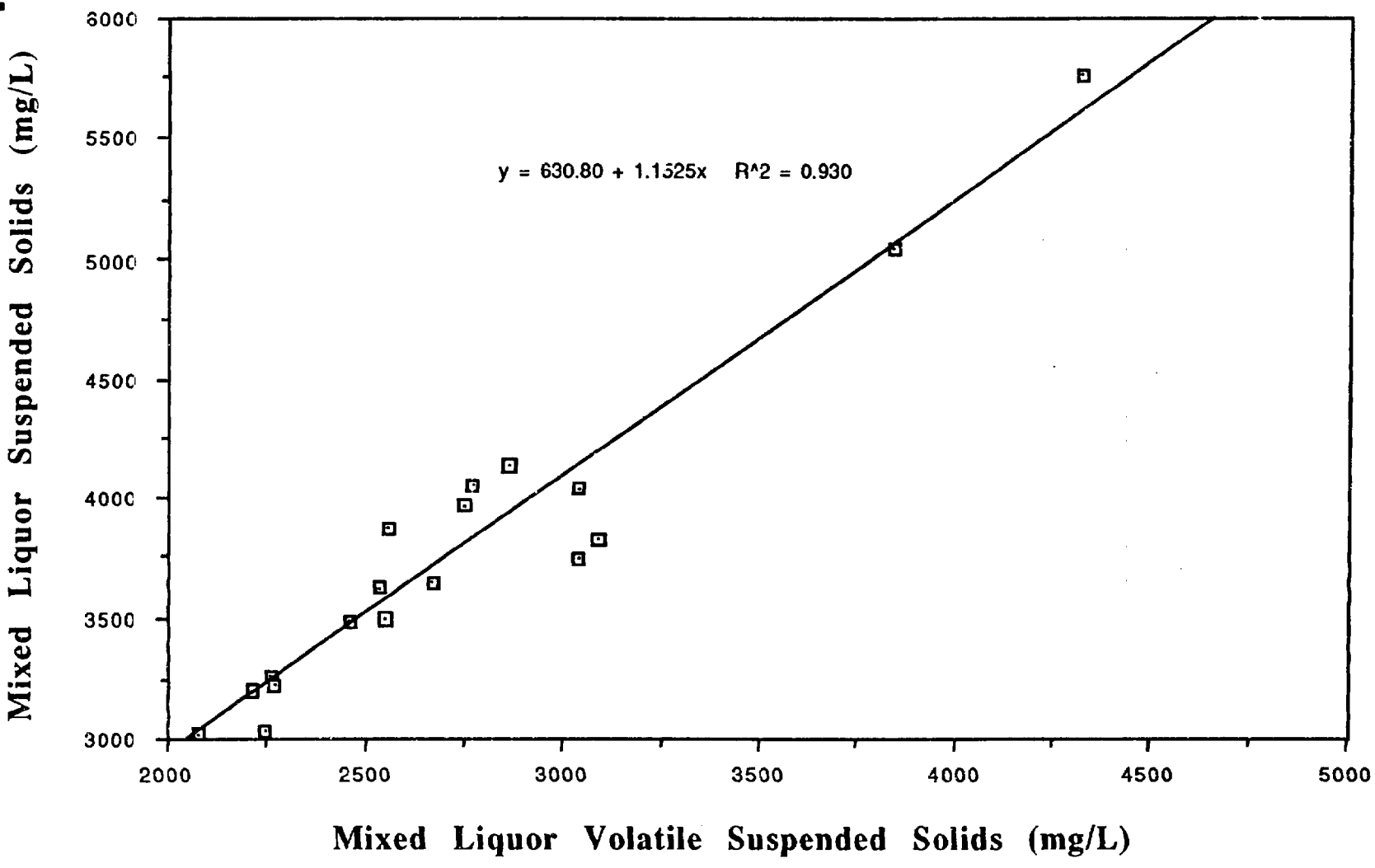
Source: Arthur D. Little, Inc.

FIGURE 5.15
MLSS vs. MLVSS - SBR



Source: Arthur D. Little, Inc.

FIGURE 5.16
MLSS vs. MLVSS - Extended Aeration



Source: Arthur D. Little, Inc.

decline as soon as NG was introduced to the system. NG not only appears to have suppressed the protozoan populations, but it also inhibited the growth and survival of the bacteria.

5.5.2 DBP and DPA Concentration in Biomass

Currently, the EPA considers all sludges generated in the treatment of wastewaters from the manufacturing and processing of explosives, a hazardous waste (K044, EPA Section 261.31 and 261.32 of 40 CFR Part 261), and, as such, it must be disposed of in an approved hazardous waste landfill. In this regard, any waste biological sludge produced in the treatment of ball powder propellant wastewater must be considered a hazardous waste unless specifically delisted. In order to investigate the possibility for delisting the biological sludge, a sampling and analysis program would have to be implemented to test the sludge from the full-scale biological treatment system following its installation and startup at Badger AAP. It would be necessary to analyze the sludge for various hazardous constituents (specifically NG, NDPA, DPA and DBP). However, during the biological wastewater treatment pilot-scale testing, the potential for delisting the biological sludge was examined by analyzing the sludge for NG, DPA, NDPA and DBP.

In order to examine the potential for delisting the biological sludge, it was necessary to predict the leachate concentration of the hazardous constituents in groundwater at the regulatory compliance point from the landfill where the sludge would be disposed. This concentration was calculated using the total concentration of the organic compound (DPA or DBP) in the sludge and the Organic Leachate Model published in the Federal Register, Vol. 51, Thursday, November 13, 1986, page 41088. The EPA Vertical-Horizontal Spread (VHS) model was then applied to determine the groundwater concentration at the compliance point from the landfill. Since the size of the Badger AAP landfill is an unknown, two different sizes were assumed; a large landfill of greater than 5,000 cubic yards (worst case scenario) and a small landfill of less than 500 cubic yards.

The delisting Regulatory Health Based Standards for the organic compounds of interest are:

Constituent	Limit
DPA:	1 ppm
Nitroso-DPA:	0.0071 ppm
DBP:	3.5 ppm

Using these limits and the calculation method listed above (assuming a large landfill), the total organic compound concentrations allowed in the biological sludge would be:

Constituent	Maximum Alloweble Concentration
DPA:	10,000 ppm
Nitroso-DPA:	11 ppm
DBP:	50,000 ppm

The actual concentrations found in the biological sludge generated from the NG run are:

Constituent	Actual Concentration or Range	Number of Samples
DPA:	<7.5 ppm	5
Nitroso-DPA:	(36.5-41.6) ppm	5
DBP:	<7.5 ppm	5

The values for DPA and DBP are well below the calculated allowable concentrations. However, the measured NDPA values in the sludge are above the allowable concentration (factor of 3-4 x). The levels of NDPA in the effluent and biomass are high compared to when no NG was present, indicating the biomass' inability to degrade this pollutant due to the toxic effect of the NG. In addition, significant levels of NG were found in the biomass (550-573 ppm for 5 samples). Also, high

concentrations of NG were found in the effluent indicating that the bacteria were not able to degrade NG at the current inlet concentration. Therefore, the results from the analysis of the biomass indicate that the sludge from a full-scale biological system would not be able to be delisted if NG was in the feed, because of the concentrations of NDPA and NG in the sludge.

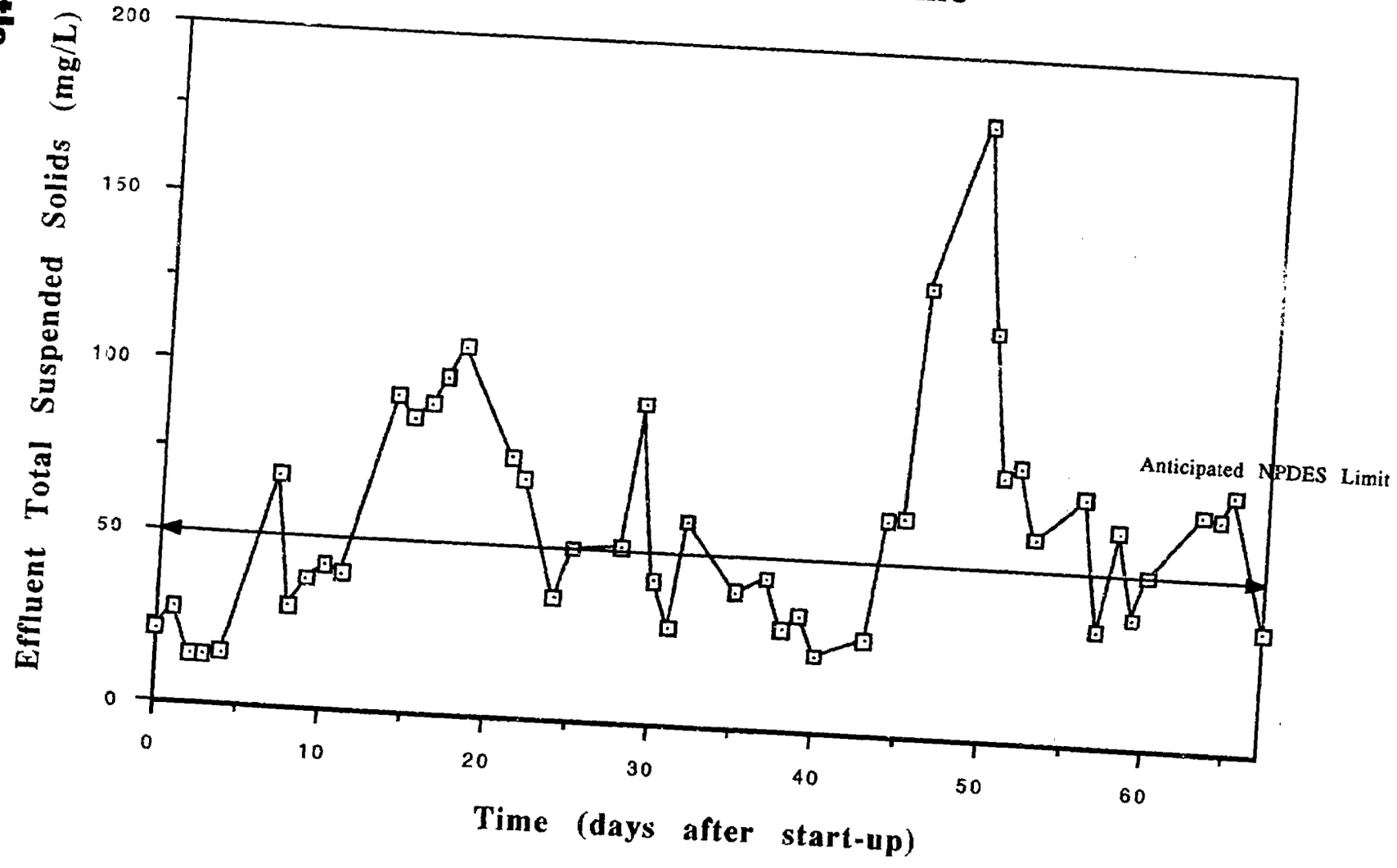
5.5.3 Biomass Settling

The settleability of the biomass is an important factor in determining the success of an activated sludge treatment system because it directly affects the total suspended solids concentration in the effluent. In Runs 1 and 2, it was observed that during optimum operating conditions the biomass settled to a uniform blanket at the bottom of the clarifier (or reactor in the case of the SBR) with a clear supernate sharply defined above it. The settleability was occasionally upset by a rapid change in operating conditions, such as altering food to mass ratios between runs or shock testing. This usually resulted in a more dispersed sludge blanket, a cloudy supernate, and an increase in total suspended solids in the effluent; all signs of an unstable system.

During the NG test runs there was a continuous problem with biomass settleability. The effluent was always cloudy and there was never a clearly defined sludge blanket. There was also a constant scum layer consisting of dead biomass floating on the surface of the reactor and the clarifier. Because the NG was found to be toxic to the bacteria at the concentrations used during the test program, the system was never able to reach stability and achieve a good settleability.

Figure 5.17 shows there were many excursions above the anticipated NPDES limit for total suspended solids in the effluent. One can see that between day 33 and day 42 (Figure 5.17) when no nitroglycerin was present in the wastewater, the reactor began to stabilize as the biomass began to thrive thereby lowering the TSS concentrations in the effluent. After day 42 when NG was again added, the TSS concentrations began to climb in the effluent as the biomass, again, began to die.

FIGURE 5.17
Effluent TSS vs. Time



Source: Arthur D. Little, Inc.

5.5.4 Biomass Production

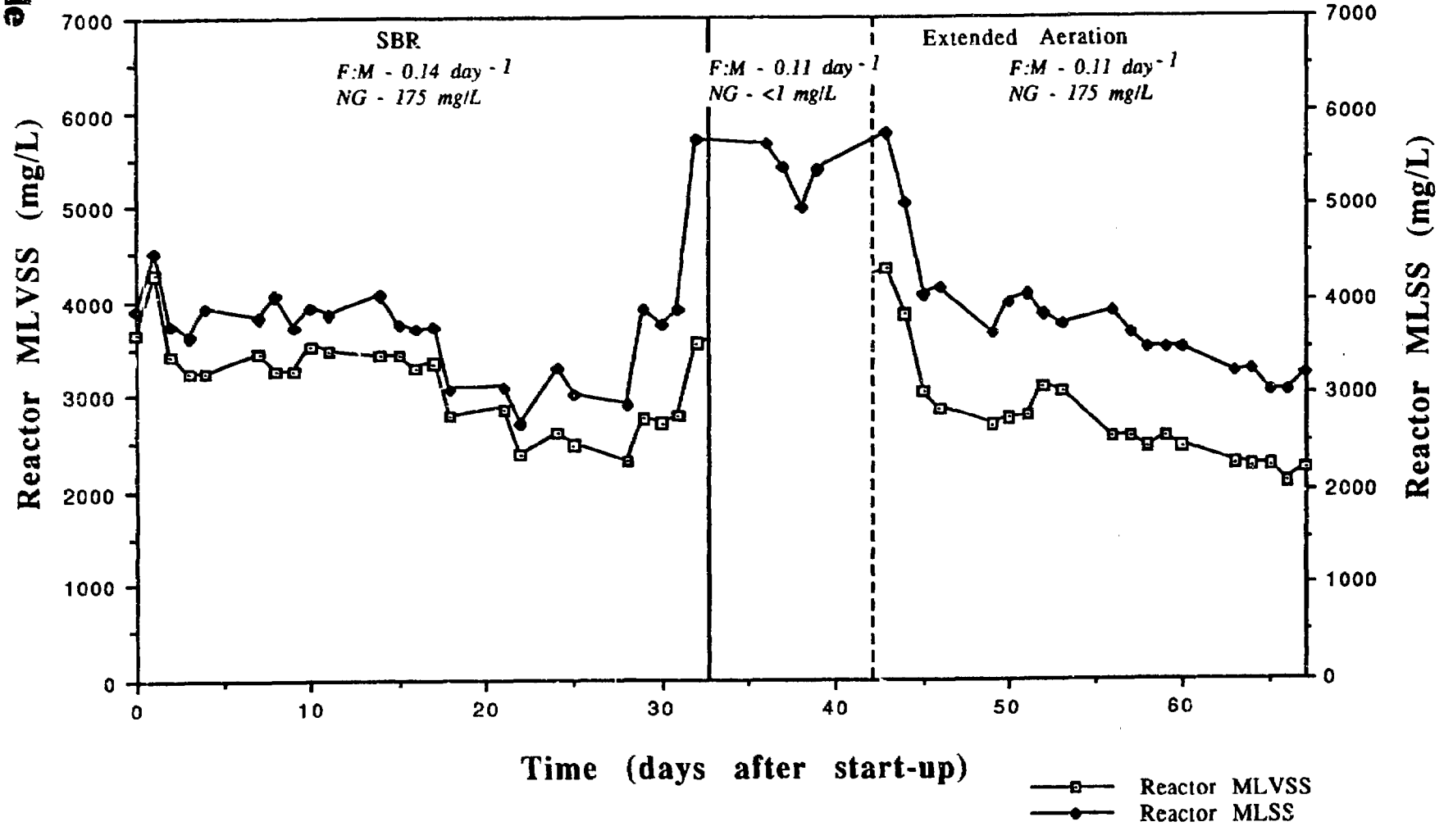
When microorganisms remove BOD from wastewater, the amount of activated sludge increases due to the growth of the biomass. In order to achieve steady state conditions in the reactor, one must continually remove an amount of biomass equal to that amount newly produced each day. Consequently, it is necessary to determine the growth rate of the biomass defined as the increase in the amount of activated sludge over a 24-hour period.

During Runs 1 and 2 at the Badger AAP pilot-scale wastewater treatment facility, the growth rate was calculated using the slopes from the MLSS graph. The positive slopes represented unhindered growth of the biomass and the negative slopes represented a sludge wasting process. The growth rates ranged from 46,000 to 56,000 mg biomass produced per day or 0.16 to 0.38 mg biomass produced per mg BOD fed.

During the NG test run there was little or no growth of the biomass, as can be seen in Figure 5.18. The MLSS concentrations fluctuate slightly, but always in a downward trend and it was unnecessary to do any sludge wasting during this test period. Figure 5.18 also shows that at day 30 when NG was removed from the wastewater feed, the biomass growth rate increased dramatically, again revealing the toxic effect NG has on the microorganisms living in the sludge.

Additional evidence of NG toxicity is the depressed dissolved oxygen uptake rate noted during this test period. In many instances, it was impossible to analyze for an actual rate because the DO uptake fell so far short of a detectable range for the test.

FIGURE 5.18
MLVSS and MLSS vs. Time



Source: Arthur D. Little, Inc.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The objectives of the pilot test program were to determine: (1) the ability of both extended aeration and SBR systems to produce a treated wastewater capable of meeting anticipated NPDES requirements when the ball powder wastewater contained NG; and (2) a better estimate of the actual concentration of NG likely to be in the wastewater. Characterization of the ball powder wastewater stream showed an average NG inlet concentration of 192 mg/L. Pilot test results indicated that NG had a toxic effect on the biomass; and, therefore, neither system was able to consistently meet anticipated NPDES limits. For a ten-day period at the beginning of the extended aeration test phase, NG was omitted from the wastewater. During this period, the analytes of concern (BOD, TSS, DPA, NDPA and DBP) were either below anticipated NPDES limits or trending downward. Based on these results, we concluded that NG at a concentration of 150 to 200 mg/L caused a toxic effect on the biomass, and we recommended that two further areas be investigated involving: 1) the identification and evaluation of technologies to pretreat ball powder wastewater to remove NG prior to aerobic biological oxidation treatment; and 2) bench- and/or pilot-scale testing to determine the toxicity limit of NG on biological treatment systems.

To assist the reader in his or her review of the NG pilot test results, we have summarized the major conclusions below:

System Performance

- Ball powder wastewater exhibited significant compositional changes over the seven days of storage; in particular, reductions in ethyl acetate, DBP, DPA, NDPA and BOD concentrations of 45, 65, 6, 60, and 25%, respectively, along with a considerable (22%) increase in the concentration of NH_3-N.

- The SBR system was capable of meeting anticipated NPDES requirements for daily BOD, DBP and NO_3-N when NG was present in the feed.

- The SBR system was not capable of meeting NPDES requirements for average BOD, TSS and NDPA when NG was present in the feed.

- The extended aeration system was capable of meeting the NPDES requirements for DBP and NO_3-N when NG was present in the feed.

- The extended aeration system was not capable of meeting the NPDES requirements for BOD, TSS and NDPA when NG was present in the feed.

Toxicity Effects

- NG in the range of 150 to 200 mg/L exhibited a toxic effect on the biomass.

- The toxic effect caused the following problems:

  - Decreased removal of BOD;
  - Inability to degrade NDPA;
  - High TSS in the effluent; and
  - Steady decrease in MLSS with time.

Recommendations

- Prior to biologically treating the ball powder wastewater, it must be pretreated to remove the NG.

- Further testing should be performed to determine the toxic limit of NG on biological treatment systems, and to develop a new or prove-out an existing pretreatment system to remove NG from the ball powder wastewater.

- Preliminary full-scale designs (both SBR and Extended Aeration) should be completed based on the design criteria developed in Runs 1 and 2; thus assuming pretreatment for NG removal.

7.0 REFERENCES

1. Olin Corporation Defense Products, "Point Source Pollution Survey Ball Powder Propellant Area," Olin Corporation, Badger Army Ammunition Plant, Baraboo, Wisconsin, 1984.

2. Wendt, T. M., J. H. Cornell, and A. M. Kaplan, "Microbial Degradation of Glycerol Nitrates," Applied Environmental Microbiology, 36:693-699, 1978.

3. Spanggord, R. J., T. Mill, T. W. Chon, W. R. Mabey, J. H. Smith, and S. Lee, "Environmental Fate Studies on Certain Munition Wastewater Constituents," ADA099256, SRI International, Menlo Park, CA, DMAD-17-78-C-8081, 1980.

4. "Ball Powder Production Wastewater Laboratory-Scale Biodegradation Support Studies," Prepared by Arthur D. Little, Inc., for USATHAMA Contract No. DAAK11-80-D-0008, May, 1987.

5. "Ball Powder Production Wastewater Pilot-Scale Biodegradation Support Studies-Test Plan," Prepared by Arthur D. Little, Inc., for USATHAMA Contract No. DAAK11-85-D-0008, June, 1987.

6. "Ball Powder Production Wastewater Pilot-Scale Biodegradation Support Studies," Prepared by Arthur D. Little, Inc., for USATHAMA Contract No. DAAK11-85-D-0008, Report No. CETHA-TE-CR-88344, February 1989.

Appendix A
Compositional Change in Wastewater Characterization over Seven Day Period

APPENDIX A

LIST OF TABLES

TABLE A.1
Change in BOD During Seven Day Holding Period

Week End Date MM/DD/YY	Initial BOD (mg/L)	Final BOD (mg/L)	Percent Reduction
08/06/88	640	520	18.75
08/13/88	780	490	37.18
08/20/88	730	680	6.85
08/27/88	670	580	13.43
09/17/88	800	640	20.00
09/24/88	800	478	40.25
10/01/88	900	579	35.67
AVERAGE	760	567	25.43

Source: Arthur D. Little

TABLE A.2
Change in COD During Seven Day Holding Period

Week End Date MM/DD/YY	Initial COD (mg/L)	Final COD (mg/L)	Percent Reduction
08/06/88	1220	923	24.34
08/13/88	1330	862	35.19
08/20/88	1163	1030	11.44
08/27/88	1112	1090	1.98
09/17/88	1240	980	20.97
09/24/88	1165	993	14.76
10/01/88	1210	804	33.55
AVERAGE	1206	955	20.83

Source: Arthur D. Little

TABLE A.3
Change in DBP During Seven Day Holding Period

Week End Date MM/DD/YY	Initial DBP (µg/L)	Final DBP (µg/L)	Percent Reduction
08/13/88	730	238	67.40
08/20/88	627	360	42.58
08/27/88	742	558	24.80
09/17/88	530	3.0	99.43
09/24/88	341	59.3	82.61
10/01/88	514	3.0	99.42
AVERAGE	581	204	64.95

Sourcer: Arthur D. Little

TABLE A.4
Change in DPA During Seven Day Holding Period

Week End Date MM/DD/YY	Initial DPA (µg/L)	Final DPA (µg/L)	Percent Reduction
08/06/88	2500	1760	29.60
08/13/88	1980	1950	1.52
08/20/88	2440	2330	4.51
08/27/88	2520	2320	7.94
09/17/88	1800	1660	7.78
09/24/88	2010	2660	-32.34
10/01/88	2320	1950	15.95
AVERAGE	2224	2090	6.04

Source: Arthur D. Little

TABLE A.5
Change in nDPA During Seven Day Holding Period

Week End Date MM/DD/YY	Initial nDPA (µg/L)	Final nDPA (µg/L)	Percent Reduction
08/06/88	105	60.0	42.86
08/13/88	189	41.1	78.25
08/20/88	151	60.0	60.26
08/27/88	229	160	30.13
09/17/88	434	112	74.19
09/24/88	192	169	11.98
10/01/88	293	42.0	85.67
AVERAGE	228	92.0	59.57

Source: Arthur D. Little

TABLE A.6
Change in EA During Seven Day Holding Period

Week End Date MM/DD/YY	Initial EA (mg/L)	Final EA (mg/L)	Percent Reduction
08/06/88	264	95	64.02
08/13/88	203	87	57.14
08/20/88	236	127	46.19
08/27/88	264	207	21.59
09/17/88	306	209	31.70
09/24/88	210	89	57.62
AVERAGE	247	136	45.11

Source: Arthur D. Little

TABLE A-7
Change in NG During Seven Day Holding Period

Week End Date MM/DD/YY	Initial NG (mg/L)	Final NG (mg/L)	Percent Reduction
08/06/88	191	173	9.42
08/13/88	179	126	29.61
08/20/88	177	165	6.78
08/27/88	212	165	22.17
09/17/88	183	183	0.00
09/24/88	214	199	7.01
AVERAGE	193	169	12.54

Source: Arthur D. Little

TABLE A.8
Change in NO3 During Seven Day Holding Period

Week End Date MM/DD/YY	Initial NO3 (mg/L)	Final NO3 (mg/L)	Percent Reduction
08/06/88	34.4	28.4	17.44
08/13/88	27.4	27.0	1.46
08/20/88	28.0	29.2	-4.29
08/27/88	29.0	30.4	-4.83
09/17/88	33.6	19.6	41.67
09/24/88	32.0	27.4	14.38
10/01/88	35.0	28.0	20.00
AVERAGE	31	27	13.40

Source: Arthur D. Little

TABLE A.9
Change in NH3 During Seven Day Holding Period

Week End Date MM/DD/YY	Initial NH3 (mg/L)	Final NH3 (mg/L)	Percent Reduction
08/06/88	5.6	4.5	19.64
08/13/88	6.0	4.5	25.00
08/20/88	4.1	4.5	-9.76
09/17/88	2.3	4.9	-111.21
09/24/88	5.5	7.9	-43.96
10/01/88	5.3	8.7	-64.91
AVERAGE	5	6	-21.61

Source: Arthur D. Little

TABLE A.10
Change in TKN During Seven Day Holding Period

Week End Date MM/DD/YY	Initial TKN (mg/L)	Final TKN (mg/L)	Percent Reduction
08/06/88	59.7	60.2	-0.84
08/13/88	54.8	52.5	4.20
08/20/88	53.0	52.4	1.13
09/24/88	65.4	65.2	0.31
10/01/88	60.6	55.8	7.92
AVERAGE	59	57	2.52

Source: Arthur D. Little

TABLE A.11
Change in TDS During Seven Day Holding Period

Week End Date MM/DD/YY	Initial TDS (mg/L)	Final TDS (mg/L)	Percent Reduction
08/06/88	3850	3920	-1.82
08/13/88	3990	3934	1.40
08/20/88	3780	3660	3.17
08/27/88	3945	3715	5.83
09/17/88	3890	2926	24.78
09/24/88	3360	3910	-16.37
10/01/88	3660	3820	-4.37
AVERAGE	3782	3698	2.23

Source: Arthur D. Little

Appendix B
Sequencing Batch Reactor Raw Data

APPENDIX B

LIST OF TABLES

APPENDIX B

LIST OF TABLES (continued)

TABLE B.1
BOD Results for Sequencing Batch Reactor With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Reactor		Effluent	
		Sample Number	BOD (mg/L)	Sample Number	BOD (mg/L)	Sample Number	BOD (mg/L)
08/01/88	0	110Y	710	112Y	9	114Y	8
08/02/88	1	120Y	640	122Y	8	124Y	8
08/03/88	2	128Y	650	130Y	3	132Y	4
08/04/88	3	138Y	840	140Y	4	142Y	8
08/05/88	4	147Y	840	149Y	7	151Y	29
08/08/88	7	157Y	520	159Y	9	161Y	21
08/09/88	8	172Y	780	174Y	5	176Y	16
08/10/88	9	181Y	860	183Y	10	185Y	25
08/11/88	10	190Y	830	192Y	30	194Y	23
08/12/88	11	204Y	750	206Y	7	208Y	28
08/15/88	14	220Y	490	222Y	6	224Y	25
08/16/88	15	239Y	730	241Y	6	243Y	28
08/17/88	16	251Y	675	253Y	12	255Y	25
08/18/88	17	263Y	655	265Y	8	267Y	34
08/19/88	18	273Y	630	275Y	2	277Y	28
08/22/88	21	292Y	680	294Y	2	296Y	14
08/23/88	22	309Y	670	311Y	9	313Y	12
08/24/88	23	325Y	600	NS		NS	
08/25/88	24	330Y	630	332Y	6	334Y	20
08/26/88	25	344Y	580	346Y	8	348Y	12
08/29/88	28	359Y	1170	361Y	6	363Y	16
08/30/88	29	376Y	1370	378Y	5	380Y	23
08/31/88	30	385Y	1440	387Y	7	389Y	14
09/01/88	31	397Y	1090	399Y	7	401Y	18
09/02/88	32	407Y	1100	409Y	12	411Y	8

Source: Arthur D. Little

TABLE B.2
COD Results for Sequencing Batch Reactor With Nitroglycerin

		Inlet		Reactor		Effluent	
Date (MM/DD/YY)	Day After Startup	Sample Number	COD (mg/L)	Sample Number	COD (mg/L)	Sample Number	COD (mg/L)
08/01/88	0	111Y	1130	112Y	113	115Y	134
08/02/88	1	121Y	1220	122Y	121	125Y	168
08/03/88	2	129Y	1090	130Y	140	133Y	170
08/04/88	3	139Y	1173	140Y	138	143Y	161
08/05/88	4	148Y	1125	149Y	181	152Y	189
08/08/88	7	158Y	923	159Y	160	162Y	250
08/09/88	8	173Y	1330	174Y	152	177Y	194
08/10/88	9	182Y	1226	183Y	153	186Y	211
08/11/88	10	191Y	1120	192Y	166	195Y	202
08/12/88	11	205Y	1130	206Y	93	209Y	249
08/15/88	14	221Y	862	222Y	158	225Y	265
08/16/88	15	240Y	1163	241Y	155	244Y	256
08/17/88	16	252Y	1098	253Y	155	256Y	250
08/18/88	17	264Y	1015	265Y	153	268Y	285
08/19/88	18	274Y	920	275Y	158	278Y	273
08/22/88	21	293Y	1030	294Y	160	297Y	222
08/23/88	22	310Y	1112	311Y	160	314Y	220
08/24/88	23	326Y	1180	NS		NS	
08/25/88	24	331Y	1118	332Y	142	335Y	184
08/26/88	25	345Y	1090	346Y	190	348Y	220
08/29/88	28	360Y	1905	361Y	152	364Y	201
08/30/88	29	377Y	1798	378Y	127	380Y	180
08/31/88	30	386Y	1798	387Y	127	390Y	70
09/01/88	31	398Y	1925	399Y	134	402Y	176
09/02/88	32	408Y	1718	409Y	181	412Y	152

Source: Arthur D. Little

TABLE B.3
DBP Results for Sequencing Batch Reactor With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	DBP (ppb)	Sample Number	DBP (ppb)
08/01/88	0	116Y	3	117Y	3
08/02/88	1	126Y	3	127Y	3
08/03/88	2	134Y	3	135Y	3
08/04/88	3	144Y	3	145Y	3
08/05/88	4	153Y	3	154Y	3
08/08/88	7	169Y	3	170Y	3
08/09/88	8	178Y	730	179Y	3
08/10/88	9	187Y	663	188Y	3
08/11/88	10	196Y	467	197Y	3
08/12/88	11	213Y	466	214Y	3
08/15/88	14	232Y	238	233Y	3
08/16/88	15	245Y	627	247Y	3
08/17/88	16	257Y	560	259Y	3
08/18/88	17	270Y	399	272Y	3
08/19/88	18	285Y	360	287Y	3
08/22/88	21	304Y	715	305Y	3
08/23/88	22	315Y	742	317Y	3
08/24/88	23	328Y	756	NS	
08/25/88	24	336Y	568	337Y	3
08/26/88	25	350Y	558	351Y	3
08/29/88	28	370Y	494	372Y	3
08/30/88	29	382Y	724	383Y	3
08/31/88	30	391Y	706	392Y	3
09/01/88	31	403Y	628	404Y	3
09/02/88	32	413Y	583	414Y	3

Source: Arthur D. Little

TABLE B.4
DPA Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	DPA (ppb)	Sample Number	DPA (ppb)
08/01/88	0	116Y	2300	117Y	4.3
08/02/88	1	126Y	2500	127Y	57.3
08/03/88	2	134Y	2400	135Y	116
08/04/88	3	144Y	1910	145Y	220
08/05/88	4	153Y	NS	154Y	240
08/08/88	7	169Y	1760	170Y	681
08/09/88	8	178Y	1980	179Y	668
08/10/88	9	187Y	2400	188Y	669
08/11/88	10	196Y	2090	197Y	33.7
08/12/88	11	213Y	2260	214Y	29.8
08/15/88	14	232Y	1950	233Y	28.7
08/16/88	15	245Y	2440	247Y	29.1
08/17/88	16	257Y	2280	259Y	18.5
08/18/88	17	270Y	1940	272Y	20.6
08/19/88	18	285Y	1910	287Y	25.5
08/22/88	21	304Y	2330	305Y	14.9
08/23/88	22	315Y	2520	317Y	25.1
08/24/88	23	327Y	2550	NS	
08/25/88	24	336Y	2160	337Y	9.2
08/26/88	25	350Y	2320	351Y	16.2
08/29/88	28	370Y	1310	372Y	26.2
08/30/88	29	382Y	1560	383Y	151
08/31/88	30	391Y	1580	392Y	172
09/01/88	31	403Y	1580	404Y	88.4
09/02/88	32	413Y	1620	414Y	40.8

Source: Arthur D. Little

TABLE B.5
nDPA Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	n-NDPA (ppb)	Sample Number	n-NDPA (ppb)
08/01/88	0	116Y	55	117Y	20
08/02/88	1	127Y	105	127Y	42
08/03/88	2	135Y	85	135Y	44
08/04/88	3	145Y	71.1	145Y	57.2
08/05/88	4	154Y	NS	154Y	49.7
08/08/88	7	170Y	62	170Y	63.4
08/09/88	8	179Y	189	179Y	66.4
08/10/88	9	188Y	161	188Y	91.2
08/11/88	10	196Y	118	197Y	75.3
08/12/88	11	213Y	102	214Y	60.1
08/15/88	14	232Y	41.1	233Y	48.2
08/16/88	15	245Y	151	247Y	42.6
08/17/88	16	257Y	93.2	259Y	50.1
08/18/88	17	270Y	67.2	272Y	40.1
08/19/88	18	285Y	60	287Y	38
08/22/88	21	306Y	157	307Y	36.7
08/23/88	22	315Y	229	317Y	25.1
08/24/88	23	327Y	226	NS	
08/25/88	24	336Y	222	337Y	80.7
08/26/88	25	350Y	160	351Y	65.4
08/29/88	28	370Y	220	372Y	90.6
08/30/88	29	382Y	295	383Y	106
08/31/88	30	391Y	254	392Y	118
09/01/88	31	403Y	197	404Y	133
09/02/88	32	413Y	172	414Y	125

Source: Arthur D. Little

TABLE B.6
Ethyl Acetate Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet	
		Sample Number	EA (mg/L)
08/01/88	0	118Y	101
08/02/88	1	119Y	264
08/03/88	2	136Y	239
08/04/88	3	NS	
08/05/88	4	146Y	119
08/08/88	7	156Y	95
08/09/88	8	171Y	203
08/10/88	9	180Y	181
08/11/88	10	189Y	194
08/12/88	11	203Y	171
08/15/88	14	219Y	87
08/16/88	15	237Y	236
08/17/88	16	249Y	179
08/18/88	17	261Y	148
08/19/88	18	282Y	127
08/22/88	21	290Y	264
08/23/88	22	308Y	220
08/24/88	23	323Y	214
08/25/88	24	329Y	225
08/26/88	25	338Y	207
08/29/88	28	357Y	643
08/30/88	29	384Y	612
08/31/88	30	393Y	616
09/01/88	31	405Y	552
09/02/88	32	415Y	405

Source: Arthur D. Little

TABLE B.7
Nitroglycerin Results for Sequencing Batch Reactor

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NG (mg/L)	Sample Number	NG (mg/L)
08/01/88	0	116Y	148	117Y	105
08/02/88	1	126Y	191	127Y	120
08/03/88	2	134Y	187	135Y	129
08/04/88	3	144Y	191	145Y	135
08/05/88	4	153Y	NS	154Y	134
08/08/88	7	169Y	173	170Y	143
08/09/88	8	178Y	179	179Y	138
08/10/88	9	187Y	171	188Y	138
08/11/88	10	196Y	178	197Y	135
08/12/88	11	213Y	175	214Y	134
08/15/88	14	232Y	126	233Y	124
08/16/88	15	245Y	177	247Y	131
08/17/88	16	257Y	176	259Y	129
08/18/88	17	269Y	173	271Y	120
08/19/88	18	284Y	165	286Y	116
08/22/88	21	304Y	184	305Y	114
08/23/88	22	315Y	212	317Y	146
08/24/88	23	327Y	210	NS	
08/25/88	24	336Y	194	337Y	125
08/26/88	25	350Y	165	351Y	134
08/29/88	28	370Y	134	372Y	147
08/30/88	29	382Y	140	383Y	114
08/31/88	30	391Y	136	392Y	91
09/01/88	31	403Y	136	404Y	78
09/02/88	32	413Y	135	414Y	69

Source: Arthur D. Little

TABLE B.8
NO3 Results for Sequencing Batch Reactor With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NO3-N (mg/L)	Sample Number	NO3-N (mg/L)
08/01/88	0	111Y	31.6	115Y	24
08/02/88	1	121Y	34.4	125Y	26.6
08/03/88	2	129Y	31.2	133Y	26.8
08/04/88	3	139Y	24.4	143Y	32
08/05/88	4	148Y	27.6	152Y	24.6
08/08/88	7	158Y	28.4	162Y	24.8
08/09/88	8	173Y	27.4	177Y	24
08/10/88	9	182Y	28	186Y	22.8
08/11/88	10	191Y	27	195Y	23.4
08/12/88	11	205Y	28.4	209Y	24.8
08/15/88	14	221Y	27	225Y	26.2
08/16/88	15	240Y	28	244Y	26.4
08/17/88	16	252Y	27.6	256Y	26.4
08/18/88	17	264Y	33.6	268Y	29.6
08/19/88	18	274Y	29.6	278Y	27.4
08/22/88	21	293Y	29.2	297Y	26.2
08/23/88	22	310Y	29	314Y	26.2
08/24/88	23	326Y	27.8	NS	
08/25/88	24	331Y	27	335Y	26
08/26/88	25	345Y	30.4	349Y	28.4
08/29/88	28	360Y	24.2	364Y	22.4
08/30/88	29	377Y	22.8	381Y	20.6
08/31/88	30	386Y	25.2	390Y	24.6
09/01/88	31	398Y	27	402Y	23.6
09/02/88	32	408Y	25.2	412Y	23.4

Source: Arthur D. Little

TABLE B.9
NH3 Results for Sequencing Batch Reactor With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NH3-N (mg/L)	Sample Number	NH3-N (mg/L)
08/01/88	0	111Y	7.6	115Y	34.8
08/03/88	2	129Y	5.6	133Y	43.3
08/05/88	4	148Y	8	152Y	43.3
08/08/88	7	158Y	10.9	162Y	42.8
08/10/88	9	182Y	4.5	186Y	41.8
08/12/88	11	205Y	6	209Y	41.5
08/15/88	14	221Y	8.3	225Y	41.8
08/17/88	16	252Y	4.5	256Y	41.6
08/19/88	18	274Y	4.1	279Y	43.7
08/22/88	21	293Y	4.2	297Y	48.4
08/24/88	23	326Y	4.8	NS	
08/26/88	25	345Y	4.5	349Y	29.8
08/29/88	28	360Y	2.21	364Y	32.8
08/31/88	30	386Y	2.96	390Y	24.6
09/02/88	32	408Y	3.9	412Y	31

Source: Arthur D. Little

TABLE B.10
TKN Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TKN (mg/L)	Sample Number	TKN (mg/L)
08/01/88	0	111Y	59.7	115Y	41.7
08/03/88	2	129Y	60	133Y	45.7
08/05/88	4	148Y	56.2	152Y	43.7
08/08/88	7	158Y	60.2	162Y	43.8
08/10/88	9	182Y	54.8	186Y	40.8
08/12/88	11	205Y	51.4	209Y	39.9
08/15/88	14	221Y	52.5	225Y	43.9
08/17/88	16	252Y	53	256Y	45.6
08/19/88	18	274Y	54.3	279Y	48.7
08/22/88	21	293Y	52.4	297Y	49.6
08/24/88	23	326Y	54.2	NS	
08/26/88	25	345Y	52.4	349Y	34
08/29/88	28	360Y	49.7	364Y	35.4
08/31/88	30	386Y	45.5	390Y	27
09/02/88	32	408Y	53	412Y	35.8

Source: Arthur D. Little

TABLE B.11
TDS Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TDS (mg/L)	Sample Number	TDS (mg/L)
08/01/88	0	110Y	3812	114Y	3544
08/03/88	2	128Y	3850	132Y	3588
08/05/88	4	147Y	3950	151Y	3650
08/08/88	7	157Y	3920	161Y	3634
08/10/88	9	181Y	3990	185Y	3500
08/12/88	11	204Y	3850	208Y	3510
08/15/88	14	220Y	3934	224Y	3690
08/17/88	16	251Y	3780	255Y	3562
08/19/88	18	273Y	3825	277Y	3490
08/22/88	21	292Y	3660	296Y	3490
08/24/88	23	325Y	3945	NS	
08/26/88	25	344Y	3715	348Y	3430
08/29/88	28	359Y	3800	363Y	3490
08/31/88	30	385Y	3735	389Y	3480
09/02/88	32	407Y	3665	411Y	3275

Source: Arthur D. Little

TABLE B.12
TSS Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TSS (mg/L)	Sample Number	TSS (mg/L)
08/01/88	0	110Y	12	114Y	22
08/02/88	1	NS		124Y	28
08/03/88	2	128Y	20	132Y	14
08/04/88	3	NS		142Y	14
08/05/88	4	147Y	15	151Y	15
08/08/88	7	157Y	11	161Y	68
08/09/88	8	NS		176Y	30
08/10/88	9	181Y	15	185Y	38
08/11/88	10	NS		194Y	42
08/12/88	11	204Y	15	208Y	40
08/15/88	14	220Y	102	224Y	104
08/16/88	15	NS		243Y	86
08/17/88	16	251Y	13	255Y	90
08/18/88	17	NS		267Y	98
08/19/88	18	273Y	20	277Y	108
08/22/88	21	292Y	26	296Y	76
08/23/88	22	NS		313Y	70
08/24/88	23	325Y	18	NS	
08/25/88	24	NS		334Y	36
08/26/88	25	344Y	12	348Y	50
08/29/88	28	359Y	16	363Y	51
08/30/88	29	NS		380Y	93
08/31/88	30	385Y	22	389Y	42
09/01/88	31	NS		401Y	29
09/02/88	32	407Y	28	411Y	59

Source: Arthur D. Little

TABLE B.13
MLSS Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Reactor	
		Sample Number	MLSS (mg/L)
08/01/88	0	113Y	3893
08/02/88	1	123Y	4510
08/03/88	2	131Y	3730
08/04/88	3	141Y	3615
08/05/88	4	150Y	3920
08/08/88	7	160Y	3820
08/09/88	8	175Y	4050
08/10/88	9	184Y	3703
08/11/88	10	193Y	3910
08/12/88	11	207Y	3850
08/15/88	14	223Y	4040
08/16/88	15	242Y	3750
08/17/88	16	254Y	3700
08/18/88	17	266Y	3707
08/19/88	18	276Y	3070
08/22/88	21	295Y	3075
08/23/88	22	312Y	2710
08/24/88	23	NS	
08/25/88	24	333Y	3280
08/26/88	25	347Y	3000
08/29/88	28	362Y	2905
08/30/88	29	379Y	3880
08/31/88	30	388Y	3745
09/01/88	31	400Y	3880
09/02/88	32	410Y	5700

Source: Arthur D. Little

TABLE B.14
MLVSS Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Reactor	
		Sample Number	MLVSS (mg/L)
08/01/88	0	113Y	3640
08/02/88	1	123Y	4260
08/03/88	2	131Y	3410
08/04/88	3	141Y	3240
08/05/88	4	150Y	3240
08/08/88	7	160Y	3440
08/09/88	8	175Y	3270
08/10/88	9	184Y	3270
08/11/88	10	193Y	3520
08/12/88	11	207Y	3470
08/15/88	14	223Y	3407
08/16/88	15	242Y	3410
08/17/88	16	254Y	3290
08/18/88	17	266Y	3340
08/19/88	18	276Y	2790
08/22/88	21	295Y	2850
08/23/88	22	312Y	2375
08/24/88	23	NS	
08/25/88	24	333Y	2605
08/26/88	25	347Y	2480
08/29/88	28	362Y	2299
08/30/88	29	379Y	2760
08/31/88	30	388Y	2700
09/01/88	31	400Y	2791
09/02/88	32	410Y	3535

Source: Arthur D. Little

TABLE B.15
Phosphorous Results for Sequencing Batch Reactor With Nitroglycerin

		Inlet		Effluent	
Date (MM/DD/YY)	Day After Startup	Sample Number	P (mg/L)	Sample Number	P (mg/L)
08/01/88	0	111Y	0.80	115Y	0.35
08/08/88	7	158Y	0.88	162Y	0.75
08/15/88	14	221Y	3.82	225Y	4.03
08/22/88	21	293Y	5.50	297Y	0.66
08/29/88	28	360Y	0.65	364Y	3.05

Source: Arthur D. Little

TABLE B.16
SO4 Results for Sequencing Batch Reactor with Nitroglycerin

		Inlet		Effluent	
Date (MM/DD/YY)	Day After Startup	Sample Number	SO4 (mg/L)	Sample Number	SO4 (mg/L)
08/03/88	2	128Y	1970	132Y	2200
08/10/88	9	181Y	1970	185Y	2100
08/17/88	16	251Y	3610	255Y	3275
08/24/88	23	331Y	2100	NS	
08/31/88	30	385Y	1800	389Y	1900

Source: Arthur D. Little

TABLE B.17
Food to Mass Ratio Results for Sequencing Batch Reactor with Nitroglycerin

Date (MM/DD/YY)	Day After Startup	F:M
08/01/88	0	0.12
08/02/88	1	0.09
08/03/88	2	0.12
08/04/88	3	0.15
08/05/88	4	0.14
08/08/88	7	0.09
08/09/88	8	0.13
08/10/88	9	0.15
08/11/88	10	0.14
08/12/88	11	0.13
08/15/88	14	0.08
08/16/88	15	0.13
08/17/88	16	0.12
08/18/88	17	0.12
08/19/88	18	0.14
08/22/88	21	0.15
08/23/88	22	0.16
08/24/88	23	NS
08/25/88	24	0.13
08/26/88	25	0.13
08/29/88	28	0.27
08/30/88	29	0.24
08/31/88	30	0.19
09/01/88	31	0.14
09/02/88	32	0.10

Source: Arthur D. Little

Appendix C
Extended Aeration Raw Data

APPENDIX C

LIST OF TABLES

TABLE C.1
BOD Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Reactor		Effluent	
		Sample Number	BOD (mg/L)	Sample Number	BOD (mg/L)	Sample Number	BOD (mg/L)
09/13/88	1	166Z	800	168Z	12	170Z	16
09/14/88	2	176Z	760	178Z	43	180Z	52
09/15/88	3	186Z	660	188Z	26	190Z	77
09/16/88	4	196Z	750	198Z	18	200Z	79
09/19/88	7	209Z	640	211Z	10	213Z	74
09/20/88	8	225Z	800	227Z	10	229Z	41
09/21/88	9	235Z	780	237Z	12	239Z	74
09/22/88	10	248Z	740	250Z	10	252Z	67
09/23/88	11	258Z	660	260Z	15	262Z	124
09/26/88	14	271Z	478	273Z	6	275Z	40
09/27/88	15	285Z	900	287Z	16	289Z	40
09/28/88	16	296Z	770	298Z	4	301Z	57
09/29/88	17	307Z	610	309Z	4	311Z	31
09/30/88	18	317Z	710	319Z	7	321Z	41
10/03/88	21	335Z	579	337Z	6	339Z	42
10/04/88	22	350Z	760	352Z	7	354Z	38
10/05/88	23	360Z	800	363Z	10	365Z	46
10/06/88	24	370Z	710	372Z	8	374Z	33
10/07/88	25	380Z	820	382Z	13	384Z	28

Source: Arthur D. Little

TABLE C.2
COD Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Reactor		Effluent	
		Sample Number	COD (mg/L)	Sample Number	COD (mg/L)	Sample Number	COD (mg/L)
09/13/88	1	167Z	1240	168Z	107	171Z	120
09/14/88	2	177Z	1250	178Z	132	181Z	170
09/15/88	3	187Z	1140	188Z	126	191Z	170
09/16/88	4	197Z	1098	198Z	126	201Z	234
09/19/88	7	210Z	980	211Z	149	214Z	266
09/20/88	8	226Z	1165	227Z	151	230Z	207
09/21/88	9	236Z	1148	237Z	173	240Z	251
09/22/88	10	249Z	1195	250Z	158	253Z	232
09/23/88	11	259Z	1150	260Z	163	263Z	251
09/26/88	14	272Z	993	273Z	160	276Z	235
09/27/88	15	286Z	1210	287Z	150	291Z	210
09/28/88	16	297Z	1220	298Z	150	301Z	230
09/29/88	17	308Z	1030	309Z	153	312Z	203
09/30/88	18	318Z	1078	319Z	160	322Z	228
10/03/88	21	336Z	804	337Z	167	340Z	250
10/04/88	22	351Z	1113	352Z	162	355Z	192
10/05/88	23	361Z	1230	363Z	162	366Z	218
10/06/88	24	371Z	1110	372Z	152	375Z	194
10/07/88	25	381Z	1020	382Z	152	385Z	182

Source: Arthur D. Little

TABLE C.3
DBP Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	DBP (ppb)	Sample Number	DBP (ppb)
09/13/88	1	172Z	530	173Z	3
09/14/88	2	182Z	30.5	183Z	3
09/15/88	3	192Z	18	193Z	3
09/16/88	4	202Z	7.9	203Z	3
09/19/88	7	221Z	3	222Z	3
09/20/88	8	231Z	341	232Z	3
09/21/88	9	244Z	389	245Z	3
09/22/88	10	254Z	256	255Z	3
09/23/88	11	264Z	228	265Z	3
09/26/88	14	283Z	59.3	284Z	3
09/27/88	15	292Z	514	293Z	3
09/28/88	16	304Z	461	305Z	3
09/29/88	17	313Z	317	314Z	3
09/30/88	18	323Z	310	324Z	3
10/03/88	21	341Z	3	342Z	3
10/04/88	22	356Z	53	357Z	3
10/05/88	23	367Z	34.2	368Z	3
10/06/88	24	376Z	7.3	377Z	3
10/07/88	25	386Z	3	387Z	3

Source: Arthur D. Little

TABLE C.4
DPA Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	DPA (ppb)	Sample Number	DPA (ppb)
09/13/88	1	172Z	1800	173Z	16.9
09/14/88	2	182Z	1650	183Z	6.5
09/15/88	3	192Z	1710	193Z	56.6
09/16/88	4	202Z	1600	203Z	71.5
09/19/88	7	221Z	1660	222Z	16.7
09/20/88	8	231Z	2010	232Z	18.9
09/21/88	9	244Z	2290	245Z	117
09/22/88	10	254Z	2430	255Z	26.8
09/23/88	11	264Z	2270	265Z	20.8
09/26/88	14	283Z	2660	284Z	14.4
09/27/88	15	292Z	2320	293Z	53.9
09/28/88	16	304Z	2220	305Z	33.6
09/29/88	17	313Z	1930	314Z	13.8
09/30/88	18	323Z	2090	324Z	13.8
10/03/88	21	341Z	1950	342Z	8.5
10/04/88	22	356Z	1610	357Z	13.7
10/05/88	23	367Z	1790	368Z	11.8
10/06/88	24	376Z	2110	377Z	20.8
10/07/88	25	386Z	2000	387Z	19.9

Source: Arthur D. Little

TABLE C.5
nDPA Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	n-NDPA (ppb)	Sample Number	n-NDPA (ppb)
09/13/88	1	172Z	434	173Z	125
09/14/88	2	182Z	281	183Z	156
09/15/88	3	192Z	236	193Z	361
09/16/88	4	202Z	192	203Z	443
09/19/88	7	221Z	112	222Z	443
09/20/88	8	231Z	192	232Z	318
09/21/88	9	244Z	203	245Z	213
09/22/88	10	254Z	191	255Z	308
09/23/88	11	264Z	154	265Z	229
09/26/88	14	283Z	169	284Z	232
09/27/88	15	292Z	293	293Z	191
09/28/88	16	304Z	196	305Z	233
09/29/88	17	313Z	144	314Z	206
09/30/88	18	323Z	103	324Z	160
10/03/88	21	341Z	42	342Z	76.4
10/04/88	22	356Z	248	357Z	141
10/05/88	23	367Z	231	368Z	31.2
10/06/88	24	376Z	226	377Z	62
10/07/88	25	386Z	157	387Z	70

Source: Arthur D. Little

TABLE C.6
Ethyl Acetate Results for Extended Aeration With Nitroglycerin

		Inlet	
Date (MM/DD/YY)	Day After Startup	Sample Number	EA (mg/L)
09/13/88	1	165Z	306
09/14/88	2	174Z	276
09/15/88	3	184Z	232
09/16/88	4	194Z	
09/19/88	7	207Z	209
09/20/88	8	223Z	210
09/21/88	9	233Z	171
09/22/88	10	246Z	200
09/23/88	11	256Z	164
09/26/88	14	269Z	89
09/27/88	15	290Z	187
09/28/88	16	294Z	
09/29/88	17	306Z	
09/30/88	18	315Z	
10/03/88	21	333Z	
10/04/88	22	349Z	
10/05/88	23	358Z	
10/06/88	24	369Z	
10/07/88	25	378Z	

Source: Arthur D. Little

TABLE C.7
Nitroglycerin Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NG (mg/L)	Sample Number	NG (mg/L)
09/13/88	1	172Z	183	173Z	55
09/14/88	2	182Z	191	183Z	85
09/15/88	3	192Z	191	193Z	100
09/16/88	4	202Z	188	203Z	111
09/19/88	7	221Z	183	222Z	129
09/20/88	8	231Z	214	232Z	142
09/21/88	9	244Z	213	245Z	149
09/22/88	10	254Z	209	255Z	152
09/23/88	11	264Z	210	265Z	148
09/26/88	14	283Z	199	284Z	140
09/27/88	15	292Z	186	293Z	135
09/28/88	16	304Z	199	305Z	124
09/29/88	17	313Z	196	314Z	119
09/30/88	18	323Z	189	324Z	114
10/03/88	21	341Z	11	342Z	81
10/04/88	22	356Z	169	357Z	99
10/05/88	23	367Z	164	368Z	96
10/06/88	24	376Z	160	377Z	95
10/07/88	25	386Z	155	387Z	90

Source: Arthur D. Little

TABLE C.8
NO3-N Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NO3-N (mg/L)	Sample Number	NO3-N (mg/L)
09/13/88	1	167Z	33.6	171Z	44.2
09/14/88	2	177Z	29.2	181Z	40.8
09/15/88	3	187Z	30.8	191Z	21.2
09/16/88	4	197Z	34.4	201Z	27.4
09/19/88	7	210Z	19.6	214Z	19.2
09/20/88	8	226Z	21.6	230Z	20.8
09/21/88	9	236Z	32.0	240Z	35.2
09/22/88	10	249Z	37.2	253Z	35.0
09/23/88	11	259Z	34.4	263Z	36.8
09/26/88	14	272Z	27.4	276Z	40.4
09/27/88	15	286Z	35.0	291Z	40.6
09/28/88	16	297Z	29.6	301Z	35.0
09/29/88	17	308Z	35.6	312Z	39.2
09/30/88	18	318Z	29.6	322Z	38.8
10/03/88	21	336Z	28.0	340Z	47.6
10/04/88	22	351Z	26.0	355Z	43.4
10/05/88	23	361Z	30.4	366Z	42.0
10/06/88	24	371Z	28.8	375Z	44.2
10/07/88	25	381Z	30.0	385Z	45.4

Source: Arthur D. Little

TABLE C.9
NH3-N Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	NH3-N (mg/L)	Sample Number	NH3-N (mg/L)
09/14/88	2	177Z	2.3	181Z	6.5
09/16/88	4	197Z	2.6	201Z	2.6
09/19/88	7	210Z	4.9	214Z	2.0
09/21/88	9	236Z	5.5	240Z	2.9
09/23/88	11	259Z	6.7	263Z	2.6
09/26/88	14	272Z	7.9	276Z	0.6
09/28/88	16	297Z	5.3	301Z	1.4
09/30/88	18	318Z	5.2	322Z	0.6
10/03/88	21	336Z	8.7	340Z	0.8
10/05/88	23	361Z	3.3	366Z	1.2
10/07/88	25	381Z	3.9	385Z	0.4

Source: Arthur D. Little

TABLE C.10
TKN Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TKN (mg/L)	Sample Number	TKN (mg/L)
09/14/88	2	177Z	54.0	181Z	12.4
09/16/88	4	197Z	64.6	201Z	11.8
09/19/88	7	210Z	62.5	214Z	9.2
09/21/88	9	236Z	65.4	240Z	11.6
09/23/88	11	259Z	49.6	263Z	14.2
09/26/88	14	272Z	65.2	276Z	8.1
09/28/88	16	297Z	60.6	301Z	7.6
09/30/88	18	318Z	57.3	322Z	8.0
10/03/88	21	336Z	55.8	340Z	9.0
10/05/88	23	361Z	59.4	366Z	10.2
10/07/88	25	381Z	57.8	385Z	4.6

Source: Arthur D. Little

TABLE C.11
TDS Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TDS (mg/L)	Sample Number	TDS (mg/L)
09/14/88	2	176Z	3890	180Z	3560
09/16/88	4	196Z	3860	200Z	3620
09/19/88	7	209Z	2926	213Z	3356
09/21/88	9	235Z	3360	239Z	3310
09/23/88	11	258Z	3440	262Z	3140
09/26/88	14	271Z	3910	275Z	3795
09/28/88	16	296Z	3660	300Z	3480
09/30/88	18	317Z	3270	321Z	3670
10/03/88	21	335Z	3820	339Z	3530
10/05/88	23	360Z	3580	365Z	3710
10/07/88	25	380Z	3710	384Z	3590

Source: Arthur D. Little

TABLE C.12
TSS Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	TSS (mg/L)	Sample Number	TSS (mg/L)
09/13/88	1	NS		170Z	28
09/14/88	2	176Z	20	180Z	63
09/15/88	3	NS		190Z	64
09/16/88	4	196Z	8	200Z	131
09/19/88	7	209Z	28	213Z	179
09/20/88	8	NS		230Z	119
09/21/88	9	235Z	5	240Z	77
09/22/88	10	NS		253Z	80
09/23/88	11	258Z	4	263Z	60
09/26/88	14	271Z	106	276Z	72
09/27/88	15	NS		291Z	34
09/28/88	16	296Z	24	301Z	63
09/29/88	17	NS		312Z	38
09/30/88	18	317Z	8	322Z	50
10/03/88	21	335Z	29	340Z	69
10/04/88	22	NS		355Z	68
10/05/88	23	361Z	22	366Z	75
10/06/88	24	NS		375Z	
10/07/88	25	380Z	8	385Z	36

Source: Arthur D. Little

TABLE C.13
MLSS Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Reactor	
		Sample Number	MLSS (mg/L)
09/13/88	1	169Z	5760
09/14/88	2	179Z	5040
09/15/88	3	189Z	4040
09/16/88	4	199Z	4130
09/19/88	7	212Z	3650
09/20/88	8	228Z	3970
09/21/88	9	238Z	4050
09/22/88	10	251Z	3830
09/23/88	11	261Z	3740
09/26/88	14	274Z	3870
09/27/88	15	288Z	3630
09/28/88	16	299Z	3480
09/29/88	17	310Z	3500
09/30/88	18	320Z	3490
10/03/88	21	338Z	3230
10/04/88	22	353Z	3260
10/05/88	23	363Z	3040
10/06/88	24	373Z	3020
10/07/88	25	383Z	3205

Source: Arthur D. Little

TABLE C.14
MLVSS Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Reactor	
		Sample Number	MLVSS (mg/L)
09/13/88	1	169Z	4320
09/14/88	2	179Z	3840
09/15/88	3	189Z	3040
09/16/88	4	199Z	2860
09/19/88	7	212Z	2670
09/20/88	8	228Z	2750
09/21/88	9	238Z	2770
09/22/88	10	251Z	3090
09/23/88	11	261Z	3037
09/26/88	14	274Z	2560
09/27/88	15	288Z	2540
09/28/88	16	299Z	2460
09/29/88	17	310Z	2550
09/30/88	18	320Z	2460
10/03/88	21	338Z	2270
10/04/88	22	353Z	2260
10/05/88	23	363Z	2245
10/06/88	24	373Z	2080
10/07/88	25	383Z	2215

Source: Arthur D. Little

TABLE C.15
Phosphorous Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	P (mg/L)	Sample Number	P (mg/L)
09/19/88	7	210Z	9.0	214Z	10.3
09/26/88	14	272Z	8.0	276Z	10.5
10/03/88	21	336Z	4.1	340Z	7.5
10/07/88	25	380Z	3.7	382Z	3.2

Source: Arthur D. Little

TABLE C.16
SO4 Results for Extended Aeration With Nitroglycerin

Date (MM/DD/YY)	Day After Startup	Inlet		Effluent	
		Sample Number	SO4 (mg/L)	Sample Number	SO4 (mg/L)
09/14/88	2	176Z	2000	180Z	2200
09/21/88	9	235Z	1700	239Z	1600
09/28/88	16	296Z	1900	300Z	2100
10/05/88	23	360Z	2150	365Z	2080

Source: Arthur D. Little

Appendix D
Analytical Methods for DPA and NDPA

APPENDIX D

TABLE OF CONTENTS

Method 625—Base/Neutrals and Acids

1. Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)[1] for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using either external or internal standard techniques with a single characteristic m/z.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 3.1.3.

3.1.1 Glassware must be scrupulously cleaned.[2] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety.

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [3-6] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composit sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used, before use, however, the compressible tubing should be throughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessores including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methlylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 µg/µL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a probelm.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 6. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality con-

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.,

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occuring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 μg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 μg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery (X) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and X with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and X for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1. The concentration of the spike in the sample should be determined as follows:

8.3.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 μg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 μg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A–B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[7] If spiking was performed at a concentration lower than 100 μg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting X' for X; (3) calculate the range for recovery at the spike concentration as (100 X'/T)±2.44(100 S'/T)%.[7]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 3.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices [8] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[9] Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH>11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K–D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K–D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K–D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K–D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K–D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.[10] Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 μL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 If the internal standard calibration procedure is being used, the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 μL of the sample extract or standard into the GC/MS system using the solvent-flush technique.[12] Smaller (1.0 μL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.
A_{is} = Area of the characteristic m/z for the internal standard.
I_s = Amount of internal standard added to each extract (μg).
V_o = Volume of water extracted (L).

15.2 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.[13] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 μg/L.[14] Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 ml.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 μL of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

References

1. 40 CFR Part 136, Appendix B.
2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.
3. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
4. "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)
8. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.
9. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
10. Eichelberger, J.W., Harris, L.E., and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectometry," *Analytical Chemistry*, 47, 995 (1975).
11. McNair, N.M. and Bonelli, E.J. "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.
12. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).
13. Olynyk, P., Budde, W.L., and Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625," Unpublished report, October 1980.
14. "Interlaboratory Method Study for EPA Method 625—Base/Neutrals, Acids, and Pesticides," Final report for EPA Contract 68-03-3102 (In preparation).

TABLE 1.—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
Chlordane	39350	57-74-9
2-Chloronaphthalene	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Dieldrin	39330	60-57-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptchlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

TABLE 1.—BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	STORET No.	CAS No.
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptchlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2

TABLE 3.—ADDITIONAL EXTRACTABLE PARAMETERS*

Parameter	STORET No.	CAS No.	Method
Benzidine	39120	92-87-5	605
β-BHC	39337	319-84-6	608
δ-BHC	39340	58-89-9	608
Endosulfan I	34361	959-98-8	608
Endosulfan II	34356	33213-65-9	608
Endrin	39390	72-20-8	608
Hexachlorocyclopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607

* See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (μg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	200
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	95	107	137
Hexachlorocyclopentadiene*	13.9		237	235	272	236	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.8	284	142	249	284	286	288
β-BHC[b]	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC[a]	22.4		183	181	109			
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I[a]	26.4		237	336	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin[a]	27.9		81	263	82			
Endosulfan II[a]	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine[a]	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde			67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethylamine[a]			42	74	44			
Chlordane[b]	19–30		373	375	377			
Toxaphene[b]	25–34		159	231	233			
PCB 1016[b]	18–30		224	260	294			
PCB 1221[b]	15–30	30	190	224	260			
PCB 1232[b]	15–32		190	224	260			
PCB 1242[b]	16–32		224	260	294			
PCB 1248[b]	18–34		294	330	262			
PCB 1254[b]	22–34	96	294	330	362			
PCB 1260[b]	23–32		330	362	394			

[a] See Section 1.2.
[b] These compounds are mixtures of various isomers. (See figures 2 thru 12.)

Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long × 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.8	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.8	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for X(µg/L)	Range for P, P, (Percent)
Acenaphthene	100	27.6	60.1–132.3	47–145
Acenaphthylene	100	40.2	53.5–126.0	33–145
Aldrin	100	39.0	7.2–152.2	D–166
Anthracene	100	32.0	43.4–118.0	27–133
Benzo(a)anthracene	100	27.6	41.8–133.0	33–143
Benzo(b)fluoranthene	100	36.8	42.0–140.4	24–159
Benzo(k)fluoranthene	100	32.3	25.2–145.7	11–162
Benzo(a)pyrene	100	38.0	31.7–148.0	17–163
Benzo(ghi)perylene	100	58.9	D–195.0	D–219
Benzyl butyl phthalate	100	23.4	D–139.9	D–152
δ-BHC	100	31.5	41.5–130.6	24–149
ε-BHC	100	21.6	D–100.0	D–110
Bis(2-chloroethyl)ether	100	55.0	42.9–126.0	12–158
Bis(2-chloroethoxy)methane	100	34.5	49.2–164.7	33–184
Bis(2-chloroisopropyl)ether	100	46.3	62.8–138.6	36–166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9–136.8	8–158
4-Bromophenyl phenyl ether	100	23.0	64.9–114.4	53–127
2-Chloronaphthalene	100	13.0	64.5–113.5	60–118
4-Chlorophenyl phenyl ether	100	33.4	38.4–144.7	25–158
Chrysene	100	48.3	44.1–139.9	17–168
4,4'-DDD	100	31.0	D–134.5	D–145
4,4'-DDE	100	32.0	19.2–119.7	4–135
4,4'-DDT	100	61.6	D–170.6	D–203
Dibenzo(a,h)anthracene	100	70.0	D–199.7	D–227
Di-n-butyl phthalate	100	18.7	8.4–111.0	1–118
1,2-Dichlorobenzene	100	30.9	48.6–112.0	32–129
1,3-Dichlorobenzene	100	41.7	16.7–153.9	D–172
1,4,-Dichlorobenzene	100	32.1	37.3–105.7	20–124
3,3'-Dichlorobenzidine	100	71.4	8.2–212.5	D–262
Dieldrin	100	30.7	44.3–119.3	29–136
Diethyl phthalate	100	26.5	D–100.0	D–114
Dimethyl phthalate	100	23.2	D–100.0	D–112
2,4-Dinitrotoluene	100	21.8	47.5–126.9	39–139
2,6-Dinitrotoluene	100	29.6	68.1–136.7	50–158
Di-n-octylphthalate	100	31.4	18.6–131.8	4–146
Endosulfan sulfate	100	16.7	D–103.5	D–107
Endrin aldehyde	100	32.5	D–188.8	D–209
Fluoranthene	100	32.8	42.9–121.3	26–137
Fluorene	100	20.7	71.6–108.4	59–121
Heptachlor	100	37.2	D–172.2	D–192
Heptachlor epoxide	100	54.7	70.9–109.4	26–155
Hexachlorobenzene	100	24.9	7.8–141.5	D–152
Hexachlorobutadiene	100	26.3	37.8–102.2	24–116
Hexachloroethane	100	24.5	55.2–100.0	40–113
Indeno(1,2,3-cd)pyrene	100	44.6	D–150.9	D–171
Isophorone	100	63.5	46.6–180.2	21–196
Naphthalene	100	30.1	35.6–119.6	21–133
Nitrobenzene	100	39.3	54.3–157.6	35–180
N-Nitrosodi-n-propylamine	100	65.4	13.6–197.9	D–230
PCB-1260	100	54.2	19.3–121.0	D–164
Phenanthrene	100	20.6	65.2–108.7	54–120
Pyrene	100	25.2	99.6–100.0	52–115
1,2,4-Trichlorobenzene	100	28.1	57.3–129.2	44–142
4-Chloro-3-methylphenol	100	37.2	40.8–127.9	22–147
2-Chlorophenol	100	28.7	36.2–120.4	23–134
2,4-Dichlorophenol	100	26.4	52.5–121.7	39–135
2,4-Dimethylphenol	100	26.1	41.8–109.0	32–119
2,4-Dinitrophenol	100	46.8	D–172.9	D–191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0–100.0	D–181
2-Nitrophenol	100	36.2	45.0–166.7	29–182
4-Nitrophenol	100	47.2	13.0–108.5	D–132
Pentachlorophenol	100	46.9	38.1–151.2	14–176
Phenol	100	22.6	16.6–100.0	5–112
2,4,6-Trichlorophenol	100	31.7	52.4–129.2	37–144

s = Standard deviation for four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

Note: These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{X}$–0.12	0.21$\bar{X}$–0.37
Acenaphthylene	0.89C+0.74	0.24$\bar{X}$–1.06	0.26$\bar{X}$–0.54
Aldrin	0.78C+1.86	0.27$\bar{X}$–1.28	0.43$\bar{X}$+1.13
Anthracene	0.80C+0.69	0.21$\bar{X}$–0.32	0.27$\bar{X}$–0.64
Benzo(a)anthracene	0.89C–0.60	0.15$\bar{X}$+0.93	0.28$\bar{X}$–0.26
Benzo(b)fluoranthene	0.93C–1.80	0.22$\bar{X}$+0.43	0.28$\bar{X}$+0.96
Benzo(k)fluoranthene	0.87C–1.06	0.19$\bar{X}$+1.03	0.35$\bar{X}$+0.40
Benzo(a)pyrene	0.90C–0.13	0.22$\bar{X}$+0.46	0.32$\bar{X}$+1.35
Benzo(ghi)perylene	0.99C–0.88	0.29$\bar{X}$+2.40	0.51$\bar{X}$–0.44
Benzyl butyl phthalate	0.99C–1.89	0.18$\bar{X}$+0.94	0.53$\bar{X}$+0.92
β-BHC	0.87C–0.94	0.20$\bar{X}$–0.56	0.30$\bar{X}$–1.94
δ-BHC	0.29C–1.09	0.34$\bar{X}$+0.86	0.93$\bar{X}$–0.17
Bis(2-chloroethyl)ether	0.99C–1.54	0.36$\bar{X}$–0.99	0.35$\bar{X}$+0.10

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Bis(2-chloroethoxy)methane	1.12C − 5.04	0.16X̄ + 1.34	0.26X̄ + 2.01
Bis(2-chloroisopropyl)ether	1.03C − 2.31	0.24X̄ + 0.28	0.25X̄ + 1.04
Bis(2-ethylhexyl)phthalate	0.64C − 1.18	0.26X̄ + 0.73	0.36X̄ + 0.67
4-Bromophenyl phenyl ether	0.91C − 1.34	0.13X̄ + 0.66	0.16X̄ + 0.66
2-Chloronaphthalene	0.89C + 0.01	0.07X̄ + 0.52	0.13X̄ + 0.34
4-Chlorophenyl phenyl ether	0.91C + 0.53	0.20X̄ − 0.94	0.30X̄ − 0.46
Chrysene	0.93C − 1.00	0.28X̄ + 0.13	0.33X̄ − 0.09
4,4'-DDD	0.56C − 0.40	0.29X̄ − 0.32	0.66X̄ − 0.96
4,4'-DDE	0.70C − 0.54	0.26X̄ − 1.17	0.39X̄ − 1.04
4,4'-DDT	0.79C − 3.28	0.42X̄ + 0.19	0.65X̄ − 0.58
Dibenzo(a,h)anthracene	0.88C + 4.72	0.30X̄ + 8.51	0.59X̄ + 0.25
Di-n-butyl phthalate	0.59C + 0.71	0.13X̄ + 1.16	0.39X̄ + 0.60
1,2-Dichlorobenzene	0.80C + 0.28	0.20X̄ + 0.47	0.24X̄ 0.39
1,3-Dichlorobenzene	0.86C − 0.70	0.25X̄ + 0.68	0.41X̄ + 0.11
1,4-Dichlorobenzene	0.73C − 1.47	0.24X̄ + 0.23	0.29X̄ + 0.36
3,3'-Dichlorobenzidine	1.23C − 12.65	0.26X̄ + 7.33	0.47X̄ + 3.45
Dieldrin	0.82C − 0.16	0.20X̄ − 0.16	0.26X̄ − 0.07
Diethyl phthalate	0.43C + 1.00	0.26X̄ + 1.44	0.52X̄ + 0.22
Dimethyl phthalate	0.20C + 1.03	0.54X̄ + 0.10	1.05X̄ − 0.92
2,4-Dinitrotoluene	0.92C − 4.81	0.12X̄ + 1.06	0.21X̄ + 1.50
2,6-Dinitrotoluene	1.06C − 3.60	0.14X̄ + 1.26	0.19X̄ + 0.35
Di-n-octylphthalate	0.76C − 0.79	0.21X̄ + 1.19	0.37X̄ + 1.19
Endosulfan sulfate	0.39C + 0.41	0.12X̄ + 2.47	0.63X̄ − 1.03
Endrin aldehyde	0.76C − 3.86	0.18X̄ + 3.91	0.73X̄ − 0.62
Fluoranthene	0.81C + 1.10	0.22X̄ − 0.73	0.28X̄ − 0.60
Fluorene	0.90C − 0.00	0.12X̄ + 0.26	0.13X̄ + 0.61
Heptachlor	0.87C − 2.97	0.24X̄ − 0.56	0.50X̄ − 0.23
Heptachlor epoxide	0.92C − 1.87	0.33X̄ − 0.46	0.28X̄ + 0.64
Hexachlorobenzene	0.74C + 0.66	0.16X̄ − 0.10	0.43X̄ − 0.52
Hexachlorobutadiene	0.71C − 1.01	0.19X̄ + 0.92	0.26X̄ + 0.49
Hexachloroethane	0.73C − 0.83	0.17X̄ + 0.67	0.17X̄ + 0.80
Indeno(1,2,3-cd)pyrene	0.78C − 3.10	0.29X̄ + 1.46	0.50X̄ + 0.44
Isophorone	1.12C + 1.41	0.27X̄ + 0.77	0.33X̄ + 0.26
Naphthalene	0.76C + 1.58	0.21X̄ − 0.41	0.30X̄ − 0.66
Nitrobenzene	1.09C − 3.05	0.19X̄ + 0.92	0.27X̄ + 0.21
N-Nitrosodi-n-propylamine	1.12C − 6.22	0.27X̄ + 0.68	0.44X̄ + 0.47
PCB-1260	0.81C − 10.86	0.35X̄ + 3.61	0.43X̄ + 1.82
Phenanthrene	0.87C − 0.06	0.12X̄ + 0.57	0.15X̄ + 0.25
Pyrene	0.64C − 0.16	0.16X̄ + 0.06	0.15X̄ + 0.31
1,2,4-Trichlorobenzene	0.94C − 0.79	0.15X̄ + 0.65	0.21X̄ + 0.39
4-Chloro-3-methylphenol	0.84C + 0.35	0.23X̄ + 0.75	0.29X̄ + 1.31
2-Chlorophenol	0.78C + 0.29	0.16X̄ + 1.46	0.28X̄ + 0.97
2,4-Dichlorophenol	0.87C + 0.13	0.15X̄ + 1.25	0.21X̄ + 1.28
2,4-Dimethylphenol	0.71C + 4.41	0.16X̄ + 1.21	0.22X̄ + 1.31
2,4-Dinitrophenol	0.81C − 18.04	0.38X̄ + 2.36	0.42X̄ + 26.29
2-Methyl-4,6-dinitrophenol	1.04C − 28.04	0.10X̄ + 42.29	0.26X̄ + 23.10
2-Nitrophenol	1.07C − 1.15	0.16X̄ + 1.94	0.27X̄ + 2.60
4-Nitrophenol	0.81C − 1.22	0.36X̄ + 2.57	0.44X̄ + 3.24
Pentachlorophenol	0.93C + 1.99	0.24X̄ + 3.03	0.30X̄ + 4.33
Phenol	0.43C + 1.26	0.26X̄ + 0.73	0.35X̄ + 0.58
2,4,6-Trichlorophenol	0.91C − 0.18	0.16X̄ + 2.22	0.22X̄ + 1.81

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of X̄, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of X̄, in µg/L.
C = True value for the concentration, in µg/L.
X̄ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol
Anthracene d_{10}	Pentafluorophenol.
Benzo(a)anthracene-d_{12}	Phenol-d_6
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol.
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2',3-Trifluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30–60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40–60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5–9 percent of mass 198.
275	10–30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443
442	Greater than 40 percent of mass 198.
443	17–23 percent of mass 442.

BILLING CODE 6560-50-M

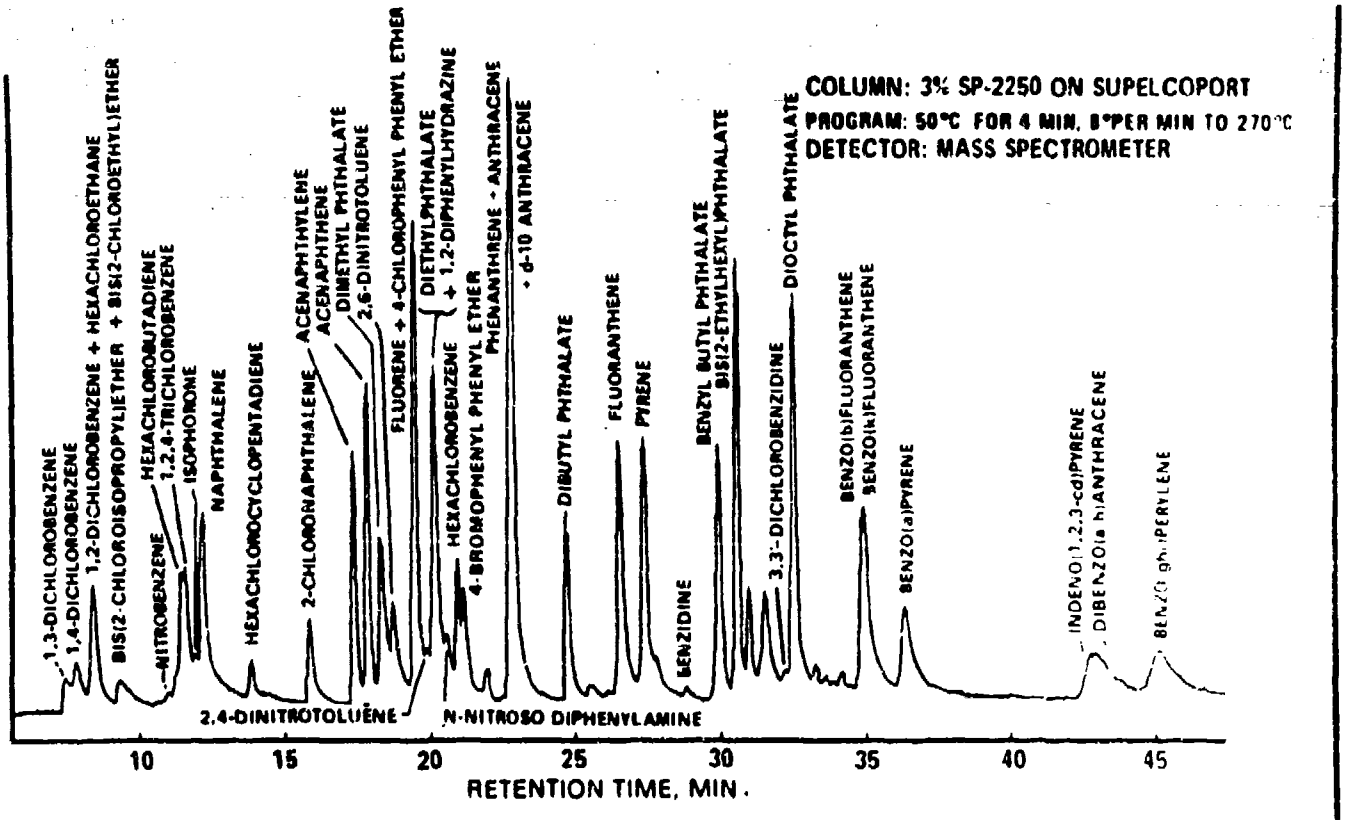


Figure 1. Gas chromatogram of base/neutral fraction.

HPLC Method for the Analysis of NDPA, DPA, DBP, and NG

1.0 SCOPE AND APPLICATION

1.1 Method used to determine the concentration of nitroglycerine, n-nitrosodiphenylamine, diphenylamine, and di-n-butylphthalate in wastewater and sludge.

2.0 SUMMARY OF METHOD

2.1 Two methods are provided for high performance liquid chromatography (HPLC) using ultraviolet (UV) detection. Method 1 detects ppm levels of nitroglycerine by direct injection of an aqueous sample into the HPLC. Method 2 detects ppb levels in aqueous samples and ppm levels in sludge samples of n-nitrosodiphenylamine, diphenylamine, and di-n-butylphthalate after appropriate sample extraction techniques are used.

3.0 MATERIALS

Filter, PTFE membrane (0.45 um), Gelman Sciences
Filter Paper, No. 41, Whatman
Glassware
- Concentrator tube, 10 mL (K-D type)
- Dispo Pipettes, 9 in,
- Drying column, 20mm ID
- Graduated Cylinders, 1000 mL
- Round Bottom Flasks, 500 mL
- Separatory funnel, 2 l with teflon stopcock
- Vials, 2 mL with teflon caps

Kuderna-Danish (K-D) apparatus
- Concentrator tube, 10 mL graduated
- Evaporation flask, 500 mL
- Snyder column, three-ball macro

Pipettes, 1.00 mL class A volumetric
Syringe, 50uL, 500 uL, and 10 mL glass, Hamilton

4.0 EQUIPMENT

A/D Converter: Hewlett Packard 18652
Disrupter Horn, No. 207 3/4 inch tapped, Ultrasonics Inc.
HPLC Column: C18 Econosil (10u, 250 X 4.6 mm), Alltech
HPLC Pump: Perkin Elmer Series 410 LC Pump
HPLC Sample autoinjector: Perkin Elmer ISS-100
pH Meter, Corning
Rotoevaporator, Bucher
Ultrasonic cell disrupter, Model W-375 Heat Systems, Ultrasonics Inc.
UV Detector: Perkin Elmer LC-95 UV/Visible Spectrophotometer

5.0 REAGENTS

Methylene Chloride, Burduck and Jackson
Methanol, Burduck and Jackson
Milli-Q H20, Millipore
Nitrogen, House Supply
Phosphoric Acid, Aldrich
Potassium Phosphate Monobasic, Cat. No. P-284, Fisher Scientific
1-Octanesulfonic Acid, Catalog No. 22,156-2, Aldrich
Sodium Sulfate, dried at 400 degrees C., Aldrich
Stock Standards
Nitroglycerin (NG), 574 ng/mL in Methanol, Received from BAAP
Ni-nitrosodiphenylamine (N-NDPA), 92+%, Lot 6-173, Chem Service
Diphenylamine (DPA), 99+%, Lot 23-15C, Chem Service
Di-n-butyl phthalate (DBP), 99.1% , Lot 23-15C, Chem Service

Calibration Standards: Calibration standards at a minimum of three concentrations levels should be prepared through dilution of the stock standards with methanol. One of the concentration levels should be at a concentration near the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in the real samples.

6.0 PROCEDURES

6.1 Procedure for Filtering Samples for Direct Injection (Method 1)

6.1.1 Fit a 10 mL glass syringe with a PTFE filter.
6.1.2 Mix the sample by shaking the container.
6.1.3 Press an aliquot of sample through the filter.
6.1.3 Collect filtrate into a 2 mL glass vial for sample custody and a 2 mL injection vial for analysis.

6.2 Procedure for Extracting Samples (Method 2)

6.2.1 Aqueous Samples

a) Pre-rinse all glassware with methylene chloride.
b) Mix sample by shaking the container.
c) Measure 1000 mL of sample into a 2 liter separatory funnel.
d) To the matrix spike sample add 1.00 mL of spiking solution.
e) Add 60 mL of methylene chloride to the separatory funnels containing samples and shake for 2 minutes. Allow the sample/solvent to partition and drain the methylene chloride into a 500 mL round bottom flask. Emulsions that form should be broken down by mechanical means only (ie. wooden stick).
f) Repeat extraction twice, combining the organic layers into the round bottom flask.
g) Rotoevaporate the extract to 20 mL. When roto-evaporating use a low water bath temperature (ie. about 35 degrees C.) and remove the sample from evaporation before it goes dry.
h) Exchange the methylene chloride extract by adding 50 mL of methanol and rotoevaporate to 2-5 mL. Transfer the extract with small amounts of methanol to a 10 mL graduated tube (K-D type).

i) Under a gentle stream of nitrogen blow the methanol extract to 1.0 mL. Caution, do not allow the sample to go dry at any point of the method.
j) Transfer the extract to a 2 mL glass vial for sample custody.
k) Prepare 10X dilutions of all samples except for the method blank by adding 450 uL methanol and 50 uL sample to a 2 mL glass vial, cap and mix.
l) Load samples into injection vials.

6.2.2 Sludge Samples

a) Determine dry weight equivalent by removing an aliquot for drying at 101 degree C. Record wet weight and dry weight.
b) Record weight of remaining sample.
c) The remaining sample is de-watered. Connect a vaccumn line to a sidearm erylenmeyer flask fitted with a fritted filter support. Place a Whatman No. 41 filter on the support and pour the sample over the entire surface of the filter paper.
d) The resultant cake is combined with sodium sulfate (previously dried) in a beaker and blended to form a free flowing consistency.
e) 150 mL of methylene chloride/acetone (1:1) is added and the sample sonicated for 1.5 minutes. Settings: 50% duty, output 8.
f) Extract is drained through a Whatman No. 4 filter paper into a 500 mL K-D flask fitted with a 10 mL concentrator tube.
g) Sonication repeated twice as in step d. Combining extracts in the K-D apparatus.
h) Extracted concentrated on a steam bath to approximately 10 mL.
i) Extract exchanged to methanol by adding 50 mL methanol and concentrating to 10.0 mL.
j) If precipitate forms filter through a PTFE membrane filter.
k) Transfer extract to a 10 mL glass tube for sample custody.
l) Load samples into injection vials.

7.0 HPLC CONDITIONS

7.1 Method 1

HPLC column	Econosil C18 (10u), 250 x 4.6 mm, Alltech
HPLC solvent	5 mM 1-Octanesulfonic acid, 5 mM Potassium Phosphate Monobasic in Methanol:Milli-Q H2O (65:35), adjusted to pH 3.0 using phosphoric acid.
Flow Rate	2.0 mL/minutes
Run Time	12 minutes
Detector settings	
Wavelength	204 nm
Response	2000 msec
Range	0.5 AUFS
Chart speed	5 mm/minute
Injection Vol	25 uL
Pressure	2600 psi

7.2 Method No. 2

HPLC column Econosil C18 (10u), 250 x 4.6 mm, Alltech
HPLC solvent 5 mM 1-Octanesulfonic acid, 5 mM Potassium Phosphate Monobasic in Methanol:Milli-Q H2O (70:30), adjusted to pH 3.0 using phosphoric acid.
Flow Rate 2.0 mL/minutes
Run Time 30 minutes
Detector settings
Wavelength 204 nm
Response 2000 msec
Range 0.2 AUFS for extracts
0.5 AUFS for diluted extracts
Chart speed 5 mm/minute
Injector Vol. 25 uL
Pressure 2400 psi

8.0 HPLC Analysis

Table 1 summarizes the retention times of components determined by this method. Figure 1 and 2 are examples of the severation achievable using the conditions given.

A minimum of three calibration standards are injected and the peaks identified. A response factor can be determined for each component at each concentration level. Samples are injected following the calibration standards and sample concentration is calculated based on the initial mean response factor. At intervals not to exceed every 10 samples a calibration standard is injected to assess instrument performance.

9.0 CALCULATIONS

$$\text{Response Factor} = \frac{\text{Response Area of Standard (A)}}{\text{Concentration of Standard (ug/mL)}}$$

$$\text{Dry Weight Equivalent} = [1 - ((W-D)/W)] \times \text{Total Sample Weight}$$

where, W = wet weight
D = dry weight

$$\text{Aqueous Sample Concentration} = \frac{(SA/RF) \times DF \times V}{(v / 1000)}$$

$$\text{Sludge Sample Concentration} = \frac{(SA/RF) \times DF \times V}{(DW / 1000)}$$

where, SA = Response Area of Sample
RF = Mean Response Factor
DF = Dilution Factors
DW = Dry Weight Equivalent (g)
V = Final Extract Volume (mL)
v = Volume Extracted (mL)

10.0 METHOD PERFORMANCE

10.1 The method was tested by extracting reagent water spiked at three concentrations over the range of 10 to 100 ug/L. Recoveries were 101 % nitroglycerine, 94.1 % n-nitrosodiphenylamine, 96.2 % diphenylamine, and 93.2 % di-n-butylphthalate.

11.0 QUALITY ASSURANCE

11.1 Each time a set of samples are prepared a distilled water method blank should be processed. The method blank serves as a safeguard against chronic laboratory contamination.

11.2 Each time a set of samples are prepared a matrix spike sample should be processed. The matrix spike sample should contain known levels of the components to be tested. The matrix spike sample serves to monitor laboratory quality control.

11.3 The mean initial calibration response factor should not exceed a 20 % Relative Standard Deviation.

11.4 A calibration-check standard should be analyzed at a minimum frequency of once per ten samples to verify the validity of the initial calibration.

Table 1

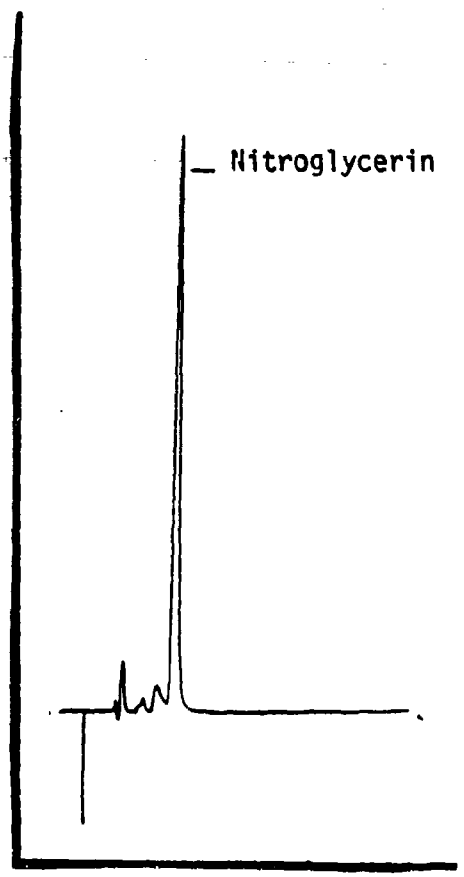
Retention Times

Component	Retention Time (min)
Method 1	
Nitroglycerine	3.33
N-nitrosodiphenylamine	NA
Diphenylamine	NA
Di-n-butylphthalate	NA
Method 2	
Nitroglycerine	NA
N-nitrosodiphenylamine	4.68
Diphenylamine	6.02
Di-n-butylphthalate	15.15

NA Not applicable.

Figure 1

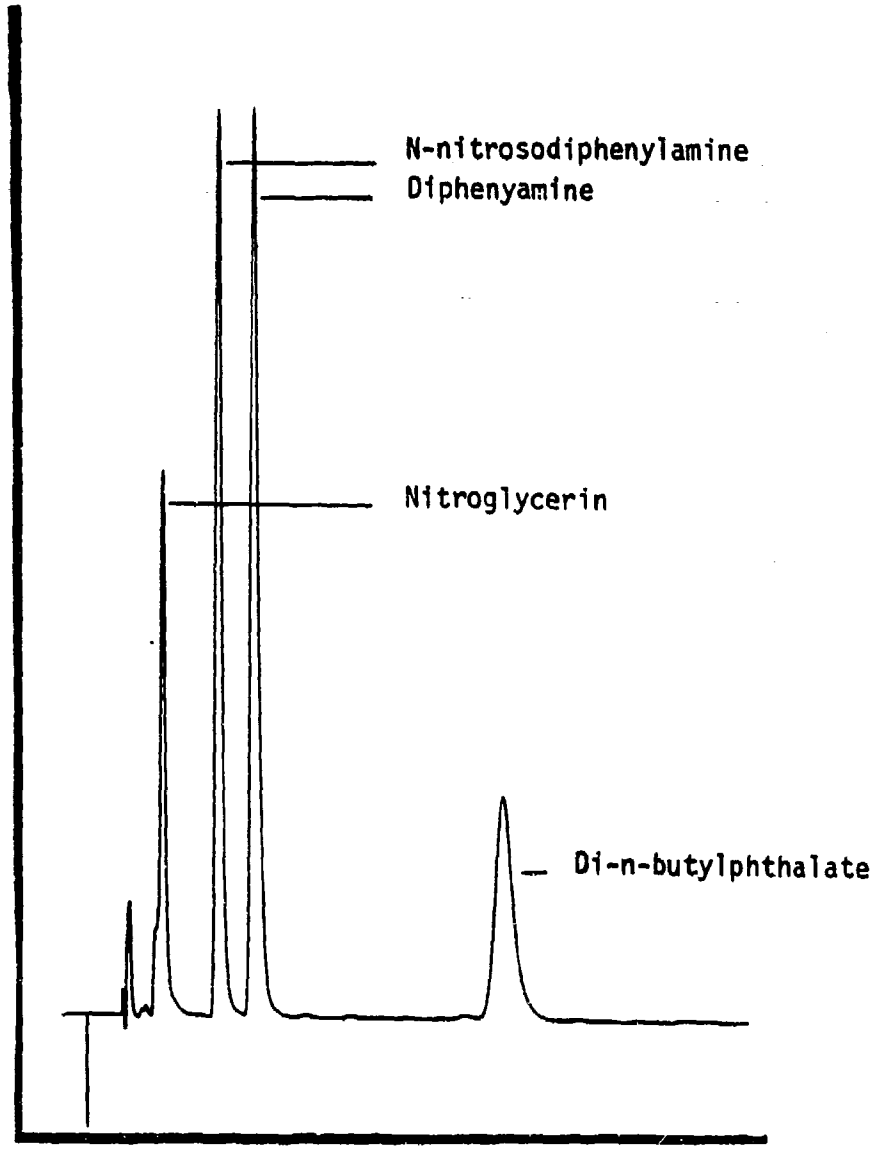
Separation of Nitroglycerine using Method 1



HPLC column	Econosil C18 (10u), 250 x 4.6 mm, Alltech
HPLC solvent	5 mM 1-Octanesulfonic acid, 5 mM Potassium Phosphate Monobasic in Methanol:Milli-Q H2O (65:35), pH 3.0
Flow Rate	2.0 mL/minutes
Run Time	12 minutes
Detector settings	
Wavelength	204 nm
Response	2000 msec
Range	0.5 AUFS
Chart speed	5 mm/minute
Injection Vol	25 uL

Figure 2

Separation Achieved using Method 2



HPLC column	Econosil C18 (10u), 250 x 4.6 mm, Alltech
HPLC solvent	5 mM 1-Octanesulfonic acid, 5 mM Potassium Phosphate Monobasic in Methanol:Milli-Q H2O (70:30), pH 3.0
Flow Rate	2.0 mL/minutes
Run Time	30 minutes
Detector settings	
Wavelength	204 nm
Response	2000 msec
Range	0.2 AUFS for extracts 0.5 AUFS for diluted extracts
Chart speed	5 mm/minute
Injector Vol.	25 uL